



UNIVERSITY HAND BOOK
of
UNDERGRADUATE CHEMISTRY EXPERIMENTS
on

Quantitative Chemical Analyses : Organic Reactions :
Chromatographic Separations & Physicochemical Experiments

for
Three-year B.Sc. General & Honours Courses.

PRINCIPLES & METHODOLOGIES

Compiled by

Prof. Sripati Bhushan Chakraborty

Dr. Dilip Kumar Hait

Dr. Subir Nath Bhattacharya

Dr. Swapan Kumar Mukherjee

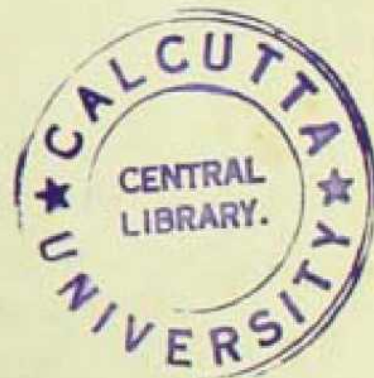
Dr. Nemaï Chand Ganguly

Dr. Rana Sen

Edited by

Prof. G. N. Mukherjee

UNIVERSITY OF CALCUTTA





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Price : Rs. 150/-

BCU 3585

GS 1869

PRINTED & PUBLISHED BY SRI PRADIP KUMAR GHOSH,
SUPERINTENDENT, CALCUTTA UNIVERSITY PRESS,
48, HAZRA ROAD, KOLKATA — 700 019



About the Contributors

Prof. Sripati Bhusan Chakraborty

Ex-Head of the Department of Chemistry (Retired)
Ramakrishna Mission Vivekananda Centenary College
Rahara, 24-Parganas, West Bengal

Dr. Dilip Kumar Hait

Teacher-in-Charge & Ex-Head of the Department of Chemistry
St. Paul's Cathedral Mission College, Kolkata

Dr. Swapan Kumar Mukherjee

Head of the Department of Chemistry
St. Paul's Cathedral Mission College, Kolkata

Dr. Nemai Chand Ganguly

Reader in Chemistry, Kalyani University

Dr. Subir Nath Bhattacharyya

Reader in Chemistry, University of Calcutta

Dr. Rana Sen,

Reader in Chemistry,
Scottish Church College, Kolkata

Editor

Prof. G. N. Mukherjee

Sir Rashbehary Ghose Professor of Chemistry
Chairman, U. G. Board of Studies in Chemistry
University of Calcutta



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9. Dr. Rathindra Nath Mukherjee, S.A. Jaipuria College, Kolkata
10. Dr. Shyamal Gangopadhyay, Dum Dum Motijhil College, Kolkata
11. Dr. Kalyan Kumar Mukherjee, F.C. College, Diamond Harbour,
(Now in Jadavpur University)



Foreword

The University Hand Book of Undergraduate Chemistry Experiments for the Three-year B.Sc. General and Honours courses is now ready for publication. This Hand Book is the product of a commendable exercise undertaken by Prof. G.N. Mukherjee and his associates.

The need for such a Hand Book was being felt for quite some time. The syllabi of the B.Sc. Chemistry Honours and General courses of this university have undergone a thorough revision in recent years. The object is to keep our students abreast of the recent developments in the subject. So far as the theoretical parts of the new syllabi are concerned, a number of good text books as well as reference books are available in the market. These, however, do not provide enough guidance to the students regarding the practical papers. Both the teachers and the students have often felt the need for a comprehensive compilation of the different types of experiment prescribed in the practical papers. This is particularly true of the experiments newly introduced in the syllabi. Unavailability of such a compilation has also made the task of ensuring uniformity of standard of teaching of these papers across the different colleges very difficult. It is hoped that this Hand Book will cater to this keenly felt need.

The University hopes to be able to publish similar compilations for other subjects where laboratory work constitutes important parts of the syllabi. I recommend the Hand Book to the teachers and students of Chemistry and I congratulate Prof. G. N. Mukherjee and his collaborators in this compilation project for a job extremely well-done.

Date : July 30, 2003.

Asis Kumar Banerjee

Vice- Chancellor



Contents

			Page
Preface			(i)-(ii)
References	(iii)
CHAPTER – 1			1
Gravimetric Estimations	
CHAPTER – 2			20
Titrimetric Estimations Based on Acidimetry & Alkalimetry	
CHAPTER – 3			28
Principles of Redox Titrimetric Analyses	
(a) Permanganometry, (b) Dichromatometry,			
(c) Iodometry & Iodimetry			
CHAPTER – 4			47
Redox Titrimetric Estimations Based on Permanganometry	
CHAPTER – 5			73
Redox Titrimetric Estimations Using Standard Potassium	
Dichromate Solution			
CHAPTER – 6			104
Titrimetric Estimations Based on Complexometric	
EDTA Titrations			
CHAPTER – 7			132
Organic Reactions	
CHAPTER – 8			160
Chromatographic Separations	
CHAPTER – 9			185
Physicochemical Experiments	
CHAPTER – 10			208
Advanced Physicochemical Experiments Involving	
Instrumental Techniques			
CHAPTER – 11			249
Titrimetric Estimations of Single Compounds / Constituents /	
Parameters			
CHAPTER – 12			298
Colourimetric Estimations	
APPENDIX			
A. Reagents Used in Quantitative Chemical Analysis	308
B. List of U.G. Experiments : Quantitative Chemical Analysis,	312
Organic Reactions, Chromatographic Separations &			
Physicochemical Experiments included in the Revised Syllabus (2002)			
of Three year (General & Honours) Degree Course in Chemistry of the			
University of Calcutta			



Preface

Chemistry curricula of Three-year B.Sc. General and Honours courses in this University have of late undergone two successive revisions. While there had been a drastic change in the course structure and modalities of evaluation both in the theoretical and practical papers in the first revision (1998-1999) to keep pace with current developments in the subject on one hand and to meet the growing demand of skilled man-power in the diversified fields of applications of Chemistry on the other, the second revision (2002) has been mainly based on the recommendations made in the model curricula formulated by the West Bengal State Council of Higher Education (2001) and the University Grants Commission, New Delhi (2001) for maintaining uniformity in the standard at the State and National Levels respectively, keeping the (1998-1999) course structure and evaluation modalities unchanged.

Although quite a good number of well written authentic text and reference books covering the course contents of the theoretical papers are available, an authentic and comprehensive compilation covering the different types of experiments in the practical papers for both General and Honours courses, particularly for the newly introduced ones and those involving instrumental techniques, chromatography and ion-exchange methods had been the most urgent need of the U. G. Chemistry community ever since the 1998-1999 syllabus was implemented. In fact, it had been difficult to maintain a uniform standard in Practical Chemistry, as were evident during the practical examinations. In view of this, the U.G. Board of Studies in Chemistry proposed to compile this "Hand Book of U. G. Chemistry Experiments on Quantitative Chemical Analyses, Organic Reactions, Chromatographic Separations & Physicochemical Experiments". Qualitative Chemical Analyses have not been included in this compilation, since many authentic guide books on these analyses are available. Moreover, the actual experimental procedures of qualitative analysis differ from sample to sample.

A panel of experts of different branches of Chemistry from among the College and University teachers associated with U. G. Chemistry practical programme and also with U. G. Chemistry practical examinations in this University and also in other Universities was recommended by the U. G. Board of Studies in Chemistry to compile the Principles and Methodologies of the experiments in order to suit the time frame of the revised curricula of U.G. Chemistry for General and Honours Courses and also that of the practical examinations. The present Hand Book is the out come of two years laboratory exercise of the contributors assisted by their colleagues and students in their respective Colleges and Universities.



However, for a multi-authored compilation like this, repetition / omission / misprints etc. may be quite often. I solicit the co-operation of all the users of this Hand-Book in pointing out such failure if any and also their valuable suggestions for further improvement of this compilation. In spite of all its shortcomings, I strongly believe this user-friendly Hand-Book will meet the long standing need of the U. G. Chemistry community.

We are grateful to the authority of the University of Calcutta for giving us the opportunity to undertake this compilation work for the benefit of our students.

We express our indebtedness to Prof. R.S. Banerjee, Dr. S. Ray and Dr. S.S. Mandal, of the Department of Chemistry, University of Calcutta; Prof. Sanjib Bagchi, of the Department of Chemistry, Burdwan University; Dr. A. V. Saha, Head of the Department of Chemistry, R.K. Mission Residential College, Narendrapur and Dr.(Mrs.) Chhanda Mukhopadhyay of the Department of Chemistry, St. Paul's Cathedral Mission College, Kolkata, for learned discussions and valuable suggestions. We are grateful to Mr. Ansuman Das and Miss Susmita Banerjee, Research Scholars in the Department of Chemistry, University of Calcutta, for computer designing of the diagrams and surveying the literature.

Our sincere thanks are due to Mr. Asit Kumar Samanta, of the Department of Chemistry, University of Calcutta, for computer composing the manuscript of this compilation.

Dated : April, 2003

*Rashbehary Shiksha Prangan
92, Acharya Prafulla Chandra Road
Kolkata - 700 009*

Prof. G. N. Mukherjee

List of Reference Books

1. Vogel's Text Book of Quantitative Inorganic Analysis including Elementary Instrumental Analysis (4th Edn.). ELBS & Longman, 1978. J. Bassett, R.C. Denney, G.H. Jeffery & J. Mendham.
2. Quantitative Inorganic Analysis – G. Charlot & D. Bezier, Translated by R. C. Murray. Methuen & Co. Ltd., London & John Wiley & Son, Inc. New York, 1957 (and references there in).
3. Quantitative Chemical Analysis – I. M. Kolthoff, E. B. Sandell, E. J. Meehan and S. Bruckenstein (4th Edn.). Macmillan, London, 1969.
4. Hand Book of Analytical Chemistry – Ju. Lurie, MIR Publishers, Moscow, 1978.
5. Volumetric Analysis – III – I. M. Kolthoff & R. Belcher with V. A. Stanger & G. Matsuyama. Interscience Publishers (a Division of John Wiley & Sons. Inc., New York, London, Sydney) 1957 (and references there in).
6. Instrumental Methods of Analysis – H. H. Wilard, L. L. Merritt, Jr. & J. A. Dean (4th Edn.). Affiliated East West Press Pvt. Ltd., New Delhi, 1965.
7. Practical Physical Chemistry – A. M. James & F. F. Prichard.
8. Findlay's Practical Physical Chemistry – B. P. Levitt.
9. Vogel's Text Book of Practical Organic Chemistry. Revised by B.S. Furniss, A.J. Hannaford, V. Rogers, P.W.G. Smith & A. R. Tatchelt.
10. Named and Miscellaneous Reactions in Practical Organic Chemistry – R.J.W. Cremllyn and R.H. Still.
11. Chemistry in the Laboratory (4th Edn.) – Julian L. Roberts, Jr. J. Leland Hollenberg, James M. Postma.



Chapter - 1

Gravimetric Estimations

General Principle :

Gravimetric analysis is the method of quantitative determination based upon weighing substances of definite composition in pure form. A known quantity of the sample solution is chemically transformed into a sparingly soluble pure stable compound, which is quantitatively precipitated and then separated from the solution by filtration, dried and weighed as such or converted into a form that has definite stoichiometry and is suitable for weighing. Frequently, the constituent being determined is weighed in a form other than that which is precipitated, when the precipitate does not have a definite stoichiometry, or, the precipitate is not stable at the drying temperature. For estimation of metals, such non-stoichiometric precipitate are often ignited to oxides of definite stoichiometry and weighed as such. Weighing should be carried out using good analytical balance with calibrated weights.

Chemical transformation of the sample in to the desired sparingly soluble product should be quantitative. Solubility of the precipitate should be so low that the quantity remaining in solution even after precipitation, filtration and washing must not exceed the minimum quantity weighable by an analytical balance i.e., 0.1 mg.

Gravimetric method of estimation depends upon the solubility product of the precipitate formed, temperature of precipitation, effects of common ions, acid-base nature of the precipitate, effect of the electrolytes in the wash liquid etc. The nature of the precipitate formed should be such that co-precipitation and post-precipitation are minimum. Purity and well defined stoichiometry of the precipitate are the primary criteria of gravimetric estimation. Contamination of precipitate may occur mainly in two ways, viz., by co-precipitation and post precipitation. These are the two sources of error in precipitation.

(i). Co-precipitation

Contamination of the precipitate by substances, which are normally soluble in the mother liquor, is termed as co-precipitation, which may occur in two ways, viz., adsorption on the surface of the precipitate exposed to the solution and occlusion of foreign substances during the process of crystal growth from the primary crystals. The ions which form the least soluble salt, is the one most strongly adsorbed by ionic lattice. For example, silver iodide adsorbs silver acetate more strongly than silver nitrate, since silver acetate is less soluble than silver nitrate.

That is why, AgI is precipitated in dilute HNO_3 medium but not in acetic acid medium. Deformability of the adsorbed ion and extent of electrolytic dissociation of the adsorbed compound also have considerable influence. H_2S is very strongly adsorbed by metallic sulphides.

The second type of co-precipitation occurs during the formation of crystalline precipitate. This may be minimised by slowing down the precipitation, which favours the formation of larger crystals. Purity of the precipitate will be quite low when large crystals are formed rapidly, where isomorphous substances are present and solid solutions are formed. As for example, BaSO_4 is contaminated by alkali nitrates.

(ii). Post-precipitation

This type of precipitation occurs on the surface of the desired precipitate. This may occur when the solution after precipitation is super saturated with some other ions which also form sparingly soluble substances. For example, in the precipitation of calcium oxalate in the presence of magnesium ion, magnesium oxalate separates slowly upon the calcium oxalate crystals. The longer the precipitate is allowed to stand in solution, the greater is the error due to post-precipitation. This may be minimised by controlling the temperature of precipitation and time for standing in contact with the mother liquor.

Influence of digestion on aging of the precipitate :

Digestion is usually carried out by allowing the precipitate to stand for definite time at room temperature, or, at a suitable higher temperature to minimise post-precipitation. Two types of changes may occur during digestion. Firstly, the smaller particles having greater solubility than the larger ones may pass into solution and may redeposit on the larger particles. Co-precipitation on smaller particles is thus eliminated. Adjustment of proper digestion temperature also reduces post-precipitation. Secondly, the irregular shaped particles possess larger surface. On digestion, these particles tend to achieve more regular shapes. As a result, the extent of adsorption decreases. Filtration is easier when larger particles are formed.

Conditions of precipitation :

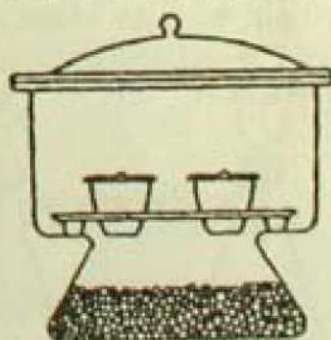
The conditions in gravimetric analysis are specific for a particular estimation and hence no general rules can be framed for complete precipitation of all the materials. However, to minimise the determinate error the following conditions may be maintained :

- a) Precipitation should be carried out in dilute solution by adding dilute solution of the precipitant to minimise co-precipitation.
- b) For growing of larger crystals, precipitation should be carried out in hot condition using a hot solution of the precipitant, provided solubility and stability of the precipitate permit. At higher temperature solubility of the precipitate is increased, chance of supersaturation is reduced, coagulation is favoured, sol formation is minimised, and crystal formation becomes rapid. As a result, regular shaped and large-sized crystals are formed.

- c) The precipitant should be added in small portions, with constant stirring using a glass rod. This favours deposition of large-sized crystalline precipitate and also minimize supersaturation of the solution.
- d) Contamination due to post-precipitation increases with length of time the precipitate is kept in contact with the mother liquor and also with agitation of the solution. The reverse is, however, true for co-precipitation.
- e) For quantitative precipitation of the desired compound, the amount of precipitant added should always be greater than the theoretical amount.
- f) The precipitate should be washed preferably with an electrolyte but not with pure water to prevent peptisation. In this operation only surface impurities are removed. The composition of the wash liquids depend upon the solubility and chemical properties of the precipitates, their tendency to peptisation, nature of the impurities to be removed and the effect of the wash liquid upon the subsequent treatment of the precipitate prior to weighing.

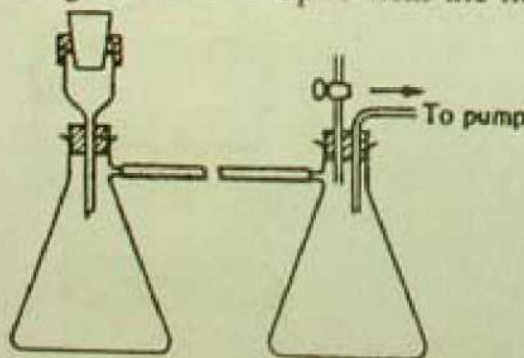
Equipment and apparatus :

- i) *Balance* : A good analytical balance with sensitivity of 0.0001 g with a weight box containing calibrated weights is essential. Single pan automatic balances are most useful for gravimetry.
- ii) *Oven* : Electric ovens with thermostatic temperature control arrangement, operating in $110^{\circ} - 180^{\circ} \text{C}$ temperature range are useful in common gravimetric analysis involving direct weighing of the precipitates.
- iii) *Furnaces* : Electrical furnaces with thermostatic temperature control arrangement operating in the temperature range $200^{\circ} - 1000^{\circ}\text{C}$ are useful for ignition of precipitates lacking in stoichiometry and unstable under drying condition.
- iv) *Desiccator* : Small to medium size (6 – 10 inch. in diameter) containing dehydrated silica gel with indicator are used for cooling the crucible containing the precipitate before weighing it after heating in the oven/furnace.



Desiccator

- v) *Glasswares* : For precipitation, beakers, clock glass, droppers, glass rod and policeman are used. Policeman is a glass rod fitted with about 1.5 cm rubber tubing. It is very useful for quantitatively transferring the precipitate from the beaker to the filtering crucible.
- vi) *Hot plate* : Electrical hot plates are used for digesting the solution at $\sim 100^{\circ} - 120^{\circ} \text{C}$.
- vii) *Water bath* : Electrically heated water baths are used for concentrating the solutions by evaporation and for settling of the precipitates in hot condition. Temperature maintained by a boiling water bath is around $80^{\circ} - 100^{\circ} \text{C}$.
- vii) *Crucibles* : (a) Silica crucibles are resistant to chemicals. These can be heated to temperature as high as $1200^{\circ} - 1500^{\circ} \text{C}$, and are suitable for ignition of the precipitates. These can be rapidly cooled, but have very little resistance to mechanical shock. These are unattacked by acids except hydrofluoric acid and phosphoric acid. But silica crucibles are attacked by alkali and basic compounds. Silica crucibles may be heated either by Bunsen burners by placing them on clean clay-pipe triangles, or by putting them in electric furnaces.
- (b) Filter crucible (Sintered glass crucibles) : These are useful for drying the precipitates which have definite stoichiometry. Pyrex and Borosil glass crucibles are available in which a bed of sintered glass of definite porosity is fused inside about 1 cm above the lower part. The porosity is etched on the outer wall of the crucible, viz. G-1, G-2, G-3 or G-4 etc., for which the pore dimensions are 100, 50, 25, and 5-10 μ respectively. ($1 \mu = 10^{-3} \text{ mm}$). Sintered glass crucibles should be cleaned with appropriate cleaning reagents before and immediately after use. Particles of dimensions larger than the pores of the crucible may be filtered conveniently. A hot mixture of sulphuric acid and chromic acid may be used for removing organic compounds from the bed of the crucible. Hot conc. HCl and hot aqua-regia ($\text{HCl} : \text{HNO}_3 = 3:1$) may also be used for cleaning the sintered glass crucible, but HF, or, any alkali solution is never used.
- (ix) *Filtering arrangement* : Filtration is done under suction employing ordinary laboratory water pump. A vacuum pump with arrangement for pressure adjustment, may also be used. A previously dried (at the desired temperature) and weighed empty sintered glass crucible is fitted air-tight with an adapter with the help of a rubber band of matching size.



Suction filtering arrangement

The funnel is then fixed with a Buchner filtering flask through a rubber cork. The stem of the funnel must extend below the side tube of the filtering flask. The filtering flask is usually connected with another safety flask of same capacity fitted with a glass safety tap to prevent back suction. The water pump is started slowly at the beginning before transferring any liquid. The precipitate along with the mother liquor is transferred into the crucible slowly, keeping the upper 1/3 rd portion of the crucible of it always empty. The precipitate may be quantitatively transferred to the crucible or to the filter paper by using a policeman while spraying with the proper wash liquid. The pressure of the suction is increased at this stage to remove the liquid as far as possible. After completion of the filtration, the safety tap is opened, the crucible is disconnected and its outer surface is cleaned, wiped out with tissue paper. The crucible containing the precipitate is then placed in air oven set at the desired temperature. After one hour, or, two, the crucible is allowed to cool in a desiccator for ~ 25 minutes and then weighed. The process of heating, cooling and weighing is repeated until two successive weights are same (or, agreeing within 0.0002 g.).

Drying and weighing of crucible :

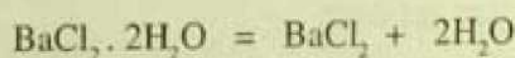
The clean empty silica crucible with its lid is placed on clay-pipe triangle and heated to dull redness for half an hour. The burner is then removed, the crucible with its lid is allowed to cool in air for ~ 1 - 2 minutes and then transferred into a desiccator using a pair of tongs and allowed to cool for ~ 25 minutes. The combined weight of the crucible with its lid is then taken. The process of heating, cooling and weighing is repeated until two consecutive weights are same (or agreeing within 0.0002 g.). The same procedure is followed for weighing of the crucible after ignition of the precipitate.

Sintered glass crucibles are without lids. These are heated in air oven at the desired temperature for ~ one hour, transferred to desiccator, cooled for ~ 25 minutes and then weighed. The process of heating, cooling and weighing is repeated until two consecutive weights are same (within ~ 0.0002 g). A similar procedure is also followed for drying the precipitate and weighing the crucible containing the precipitate.

Experiment No. 1 : Gravimetric estimation of water of crystallisation in $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$

Principle :

When $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ is heated above 100°C , anhydrous BaCl_2 results.



A known weight of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ is taken in a weighing bottle and heated in an air oven at $\sim 105^\circ\text{C}$ for one hour. After cooling in a desiccator for ~ 25 minutes, the weight of the

weighing bottle with its contents is measured. The process of heating, cooling and weighing is repeated till the two consecutive weights are same (or agreeing within 0.0002 g.).

Calculation

Let, the weight of the empty weighing bottle = W_1 g.

weight of the weighing bottle + $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ = W_2 g

weight of weighing bottle + BaCl_2 = W_3 g.

\therefore weight of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ = $(W_2 - W_1)$ g.

weight of BaCl_2 = $(W_3 - W_1)$ g.

\therefore Loss in weight = $[(W_2 - W_1) - (W_3 - W_1)] = (W_2 - W_3)$ g.

$$\therefore \% \text{ loss} = \left(\frac{W_2 - W_3}{W_2 - W_1} \right) \times 100$$

$$\therefore \text{BaCl}_2 : \text{H}_2\text{O} = \frac{(W_3 - W_1)}{\text{BaCl}_2} = \frac{(W_2 - W_3)}{\text{H}_2\text{O}}$$

$$= \frac{W_3 - W_1}{208.246} = \frac{W_2 - W_3}{18.015}$$

(Calculated : $\text{BaCl}_2 : \text{H}_2\text{O} = 1:2$)

Chemicals and Equipment :

- Barium chloride dihydrate, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (AR)
- Weighing bottle with stopper (~ 15 – 25 ml).
- Desiccator with silica gel drier.
- Air oven set at 105°C .
- Analytical balance with calibrated weight box.

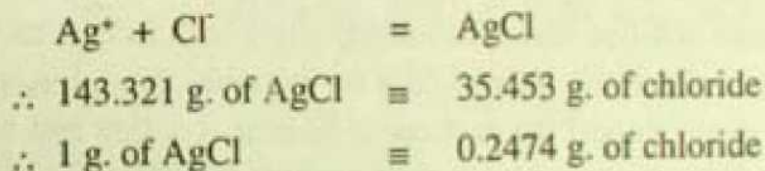
Procedure

Dry the weighing bottle with its stopper in the air oven at 105°C for one hour, cool the same for ~ 25 minutes in the desiccator and weigh the empty weighing bottle with its stopper. Repeat these operations till the two consecutive weights agree within ~ 0.2 mg. Transfer 0.5-1.0 g of the sample of A.R. $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ into the weighing bottle using a spatula and weigh the weighing bottle with its contents and the stopper. Place the weighing bottle in the air oven (105°C) with the stopper on its side over the mouth of the bottle to permit free escape of water vapour. Heat for one hour at 105°C, then stopper the bottle, place it in the desiccator and cool for ~ 25 minutes. Before weighing, loosen the stopper to equalize the pressure. Weigh the bottle with its contents keeping it stoppered during weighing. Unstopper the bottle after weighing and repeat the entire operations of heating, cooling and weighing till the two consecutive weights agree within 0.2 mg. Calculate the % of H_2O in the sample and also the ratio of $\text{BaCl}_2 : \text{H}_2\text{O}$.

Experiment No. 2 : Gravimetric estimation of chloride as AgCl

Principle:

Chloride is usually estimated as silver chloride, which is precipitated by adding an excess of AgNO_3 solution to the solution containing Cl^- ion in dilute HNO_3 medium, when AgCl (solubility product = 1.78×10^{-10}) is quantitatively precipitated.



The precipitate, which is initially colloidal in nature, is coagulated into filterable form on gentle boiling the mixture with stirring.

Chemicals and Equipment :

- ~ 0.1 (M) AgNO_3 solution : 17.0 g. lit^{-1} : Dissolve ~ 17 g. of A.R. AgNO_3 (F.W. = 169.87) in double distilled water and dilute to 1 litre. Preserve the solution in dark coloured bottle protected from light.
- ~ 0.1(M) NaCl solution : ~ 6.0 g. lit^{-1} : Dissolve ~ 6 g. (w) of A.R. NaCl in double distilled water and dilute to 1 litre. Strength = $(w/0.5844)$ (M/10).
- G-4 Sintered glass crucible
- Air oven set at 110° – 120°C
- Analytical balance with calibrated weight box
- Desiccator with silica gel drier

Procedure :

- (i) Clean the sintered-glass crucible (G-4), dry it at $110^{\circ} - 120^{\circ}\text{C}$ in an air oven for 1 hour and then allow to cool it in a desiccator for 25 minutes and weigh. Repeat the process of heating, cooling and weighing until two consecutive weights are same (or agreeing within 0.0002 g.).
- (ii) Take an aliquot of 10 ml of the sample chloride solution in a clean 250 ml beaker, dilute to 150 ml with double distilled water, add 0.5 ml of concentrated nitric acid and heat the mixture to $\sim 70^{\circ} - 80^{\circ}\text{C}$. Add 0.1 (M) AgNO_3 solution slowly with constant stirring with a clean glass rod until the formation of curdy white precipitate of AgCl is complete. Add 5 ml of AgNO_3 solution in excess. Cover the beaker partially with a clock glass, heat the suspension nearly to boiling for 2-3 minutes until the precipitate coagulates and the supernatant solution becomes clear. Check the completeness of the precipitation by adding a few drops of AgNO_3 solution to the supernatant liquid. Allow the mixture to stand for about an hour in dark.
- (iii) Fit the previously weighed sintered glass crucible with a clean Buchner funnel connected through a safety flask to the water-suction pump. Start the suction with low pressure and transfer the content in the beaker into the crucible quantitatively by washing with dilute ~ 0.01 (M) HNO_3 finally using a policeman. Wash the precipitate in the crucible 2 – 3 times with dilute ~ 0.01 (M) HNO_3 and then once with small amount of double distilled water. Dry the crucible with its contents in the air oven at $110^{\circ} - 120^{\circ}\text{C}$ for about one hour. Allow the crucible to cool in a desiccator for 25 minutes and weigh. Repeat the process of heating, cooling and weighing until two consecutive weights are same (or agreeing within 0.0002 g.).

Calculation :

Weight of empty crucible = W_1 g.

Weight of crucible + AgCl = W_2 g.

\therefore Weight of AgCl = $(W_2 - W_1)$ g.

Volume of chloride solution = 10 ml

\therefore 1 g. of $\text{AgCl} \equiv 0.2474$ g. of chloride

$\therefore (W_2 - W_1)$ g. of $\text{AgCl} \equiv (0.2474) (W_2 - W_1)$ g. of chloride in 10 ml

\therefore Strength of chloride in g/lit.

$$= (1000 \times 0.2474 (W_2 - W_1) / 10) \text{ g. lit}^{-1}$$

$$= 24.74 \times (W_2 - W_1) \text{ g. lit}^{-1}$$

Notes :

1. To minimise co-precipitation and to improve the crystalline nature of the precipitate, it is advisable to carry out the precipitation by adding the AgNO_3 to hot (70° to 80°C) solution. Heating to higher temperature may lead to loss of Cl^- as HCl .
2. AgCl is decomposed by light, so the experiment should be carried out in subdued light, the solution containing the precipitate should be kept in a dark place and the container should be covered with a piece of black paper to prevent decomposition of AgCl by sunlight.

Experiment No. 3 : Gravimetric estimation of silver as AgCl

The principle and the procedure are same as the estimation of chloride (Experiment No. 2) with the modification that a known volume (10 ml) of silver nitrate solution (containing about 0.1 g of Ag^+) is to be treated with just sufficient excess of dilute HCl under the same condition.

Calculation :

$$\therefore 143.321 \text{ g. of } \text{AgCl} \equiv 107.868 \text{ g. of } \text{Ag}$$

$$\therefore 1 \text{ g. of } \text{AgCl} \equiv 0.7526 \text{ g. of } \text{Ag}$$

$$\therefore (W_2 - W_1) \text{ g. of } \text{AgCl} \equiv 0.7526 \times (W_2 - W_1) \text{ g. of } \text{Ag in 10 ml solution.}$$

$$\therefore \text{Strength of silver solution in g.lit}^{-1}$$

$$= \frac{1000 \times 0.7526 \times (W_2 - W_1)}{10} \text{ g.lit}^{-1}$$

$$= 75.26 \times (W_2 - W_1) \text{ g. lit}^{-1}$$

Experiment No. 4 : Gravimetric estimation of sulphate as BaSO_4

Principle :

BaSO_4 (solubility product = 1.07×10^{-10}) is quantitatively precipitated when a measured volume of sulphate solution is treated with an excess of BaCl_2 solution in dil. HCl medium.



$$\therefore 233.39 \text{ g. of } \text{BaSO}_4 \equiv 96.06 \text{ g. of } \text{SO}_4^{2-}$$

$$\therefore 1.0 \text{ g of } \text{BaSO}_4 \equiv 0.4116 \text{ g. of } \text{SO}_4^{2-}$$

Therefore, by measuring the weight of BaSO_4 formed from a known volume of sulfate solution it is possible to determine the quantity of sulfate present. For quantitative precipitation of BaSO_4 , proper conditions are to be maintained to eliminate the following sources of error.

- (i) Increasing solubility of BaSO_4 in mineral acids like HCl of increasing strength due to formation of bisulphate : This may be minimised by maintaining acidity ~ 0.05 (N).
- (ii) Coprecipitation of BaCl_2 : This may be minimised by carrying out the precipitation under boiling condition.

Chemicals and Equipment :

- (i) 5% BaCl_2 solution : 5.0 g. of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ per 100 ml of double distilled water.
- (ii) Sample SO_4^{2-} solution (unknown): 12.0 g. of K_2SO_4 per 100 ml of double distilled water. Corresponding amounts of sodium or ammonium sulfate may also be used.
- (iii) G-4 Sintered glass crucible
- (iv) Air oven set at $110^\circ - 120^\circ\text{C}$
- (v) Desiccator with silica gel drier.

Procedure :

- (i) Clean the G-4 sintered glass crucible and heat it in the air oven at $110^\circ - 120^\circ\text{C}$ for an hour. Cool the crucible in a desiccator for 25 minutes and determine the weight of the empty crucible. Repeat the process of heating, cooling and weighing until two consecutive weights are same (or agree within 0.0002 g.).
- (ii) Take an aliquot of 10 ml of the sample sulphate solution in a 250 ml beaker. Add ~ 0.5 ml of concentrated hydrochloric acid and 100 ml double distilled water to adjust the acidity to ~ 0.05 (N). Heat the solution to boiling and add hot 5% aqueous BaCl_2 solution with constant stirring to completely precipitate the SO_4^{2-} as BaSO_4 . Allow the precipitate to settle in hot condition for about 5 minutes. Check the completeness of precipitation by adding a few drops of BaCl_2 solution to the clear supernatant. If there is no precipitation, add 5 ml of hot BaCl_2 solution in excess, dropwise with stirring. Cover the beaker with a clock glass and allow the mixture to settle on a hot water bath for about an hour.
- (iii) Filter the precipitate under hot condition through the previously weighed G-4 sintered glass crucible fitted with an adapter in Buchner flask using water suction pump. While washing with portions of cold water, the fine particles adhering on the side of the beaker are to be transferred into the crucible with the help of policeman. Washing is to be continued till 5 ml of the washing does not give any opalescence with a drop of

AgNO₃ solution acidified with dil HNO₃ (chloride free). Dry the crucible containing the precipitate at 110-120°C for ~ one hour, cool in a desiccator for 25 minutes and measure the weight. Repeat these operations of heating, cooling and weighing till the two consecutive weights are same (or, agreeing within 0.0002 g.).

Calculation :

$$\begin{aligned}
 \text{Weight of empty crucible} &= W_1 \text{ g.} \\
 \text{Weight of crucible + BaSO}_4 &= W_2 \text{ g.} \\
 \therefore \text{Weight of BaSO}_4 &= (W_2 - W_1) \text{ g.} \\
 \therefore 1 \text{ g. of BaSO}_4 &\equiv 0.4116 \text{ g. of SO}_4^{2-} \\
 \therefore (W_2 - W_1) \text{ g. of BaSO}_4 &\equiv 0.4116 \times (W_2 - W_1) \text{ g. of SO}_4^{2-} \\
 &\quad \text{in 10 ml solution} \\
 \therefore \text{Strength of sulfate solution in g.lit}^{-1} &= \text{Amount of SO}_4^{2-} \text{ in 1000 ml of sample solution} \\
 &= \frac{1000 \times 0.4116 \times (W_2 - W_1)}{10} \text{ g.lit}^{-1} \\
 &= 41.16 \times (W_2 - W_1) \text{ g.lit}^{-1}
 \end{aligned}$$

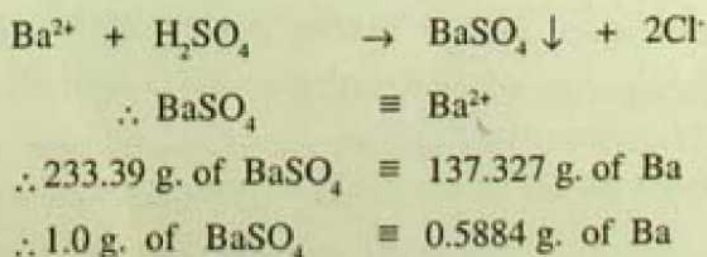
Note : During precipitation the acidity should be ~ 0.05 N. The higher acidity is avoided for enhanced solubility of BaSO₄ due to the formation of HSO₄⁻ ion.



Experiment No. 5 : Gravimetric estimation of Ba as BaSO₄

Principle :

When a known volume of Ba²⁺ solution (say BaCl₂) in dilute ~0.01 (N) HCl at ~ 80-90°C is treated with an excess of hot dilute (~ 4 N) H₂SO₄ solution, keeping the acidity below 0.05(N), BaSO₄ (solubility product 1.07 x 10⁻¹⁰) is quantitatively precipitated at nearly boiling temperature. After filtration through weighed sintered glass crucible (G-4) and washing, the precipitate is dried and weighed to constant as BaSO₄. The amount of Ba²⁺ is calculated from the weight of BaSO₄ formed.



Chemicals and Equipment :

- (i) 4 (N) H_2SO_4 solution
- (ii) ~ 1% BaCl_2 solution (unknown) : 1 g. of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ per 100 ml of H_2O .
- (iii) G-4 Sintered glass crucible
- (iv) Desiccator with silica gel drier
- (v) Analytical balance with calibrated weight box.
- (vi) Air oven set at $110 - 120^\circ\text{C}$.

Procedure :

Take an aliquot of 10 ml of the sample Ba^{2+} solution in a 250 ml beaker dilute to 100 ml with double distilled water, add 0.5 ml of concentrated hydrochloric acid. Heat the solution to boiling and add hot ($80-90^\circ\text{C}$) 4(N) H_2SO_4 dropwise with constant stirring to precipitate BaSO_4 completely. Allow the precipitate to settle for 1-2 minutes. Check the completeness of the precipitation by adding a few more drops of 4(N) H_2SO_4 solution to the clear supernatant liquid. Cover the beaker with a clock glass and allow the mixture to stand for about an hour in the hot condition on a hot water bath till the precipitate settles down giving a clear supernatant liquid. Care must be taken in bringing down the fine particles, which may skip up along the wall of the beaker.

Filter the precipitate in hot condition through a previously weighed G-4 sintered glass crucible fitted with an adapter in Buchner flask using water suction pump. Transfer the precipitate to the crucible with the aid of hot double distilled water containing a few drops of 0.1(N) sulphuric acid using a policeman to quantitatively transfer the precipitate from the beaker to the crucible. Wash the precipitate with small portions of the same hot wash liquid till the filtrate is free from chloride (test with $\text{AgNO}_3/\text{HNO}_3$ solution) then with water alone. Dry the precipitate at $110-120^\circ\text{C}$ for an hour in an air oven, cool in a desiccator for ~ 25 minutes and weigh. Repeat these operations of heating, cooling and weighing till two consecutive weights are same (or agreeing within 0.0002 g.).

Calculation :

Weight of empty crucible = W_1 g.

Weight of crucible + BaSO_4 = W_2 g.

\therefore Weight of BaSO_4 = $(W_2 - W_1)$ g.

\therefore 1 g. of BaSO_4 \equiv 0.5884 g. Ba

$\therefore (W_2 - W_1)$ g. of BaSO_4 \equiv $0.5884 \times (W_2 - W_1)$ g. of Ba in 10 ml of sample solution.

\therefore 1000 ml of Ba^{2+} solution contains

$$= \frac{1000 \times 0.5884 (W_2 - W_1)}{10} \text{ g. Ba}$$

$$= 58.84 (W_2 - W_1) \text{ g. of Ba}$$

\therefore Strength of Ba^{2+} solution = $58.84 (W_2 - W_1)$ g. of lit^{-1}

Experiment No. 6 : Gravimetric estimation of phosphate as $\text{Pb}_3(\text{PO}_4)_2$

Principle :

Lead phosphate, $\text{Pb}_3(\text{PO}_4)_2$, is sparingly soluble (solubility product = 7.94×10^{-43}). Phosphate is quantitatively precipitated as lead phosphate when a sample phosphate solution is treated with slight excess of lead acetate solution in dilute acetic acid medium.



$$\therefore \text{Pb}_3(\text{PO}_4)_2 \equiv 2\text{PO}_4^{3-}$$

$$\therefore 811.55 \text{ g. of } \text{Pb}_3(\text{PO}_4)_2 \equiv 189.94 \text{ g. of } \text{PO}_4^{3-}$$

$$\therefore 1 \text{ g. of } \text{Pb}_3(\text{PO}_4)_2 \equiv 0.234 \text{ g. of } \text{PO}_4^{3-}$$

Chemicals and Equipment :

- (i) Lead acetate solution : 10% aqueous solution.
- (ii) Glacial acetic acid
- (iii) Ammonium dihydrogen phosphate or sodium dihydrogen phosphate or disodiumhydrogen phosphate : $\sim (M/40)$ solution in double distilled water.
- (iv) G-4 Sintered glass crucible

- (v) Analytical balance with calibrated weight box.
- (vi) Desiccator with silica gel drier
- (vii) Air oven set at 110 – 120°C.

Procedure :

- (i) Clean a G-4 sintered-glass crucible, and dry it at 110° - 120°C in the air oven. Cool the crucible in a desiccator for 25 minutes and weight the empty crucible. Repeat the process of heating, cooling and weighing till the two consecutive weights agree within 0.0002 g.
- (ii) Pipette out 10 ml of the supplied solution containing phosphate into a 250 ml beaker provided with a glass rod, dilute to 100 ml with double distilled water, just neutralise with 1:1 ammonia and then acidify with 10 ml of glacial acetic acid. Heat to 70° - 80°C, add 10% lead acetate solution with constant stirring, add a slight excess of the reagent to ensure complete precipitation of lead phosphate. Cover the beaker with a clock glass and allow to stand in the hot condition for about 20 – 30 minutes. Check the completeness of precipitation by adding a few drops of the lead acetate solution to the supernatant liquid. Allow to stand for about an hour.
- (iii) Filter the cold solution through the previously dried and weighed G-4 crucible. Transfer the precipitate quantitatively by washing with cold water and using a policeman. Wash the precipitate with the cold water until the washings are free from acetate (test with AgNO_3 solution in acetic acid medium). Dry the crucible with its contents at 110° - 120°C for one hour in an air-oven at 110-120°C. Allow to cool in a desiccator for 25 minutes and then weigh. Repeat the process of heating, cooling and weighing until two consecutive weights agree within 0.0002 g.

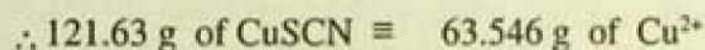
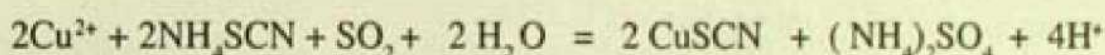
(iv) Calculation :

$$\begin{aligned}
 \text{wt. of the empty crucible} &= w_1 \text{ g.} \\
 \text{wt. of crucible} + \text{Pb}_3(\text{PO}_4)_2 &= w_2 \text{ g.} \\
 \therefore \text{wt. of Pb}_3(\text{PO}_4)_2 &= (w_2 - w_1) \text{ g.} \\
 \therefore 1 \text{ g. of Pb}_3(\text{PO}_4)_2 &\equiv 0.234 \text{ g. of PO}_4^{3-} \\
 \therefore (w_2 - w_1) \text{ g. of Pb}_3(\text{PO}_4)_2 &\equiv 0.234 (w_2 - w_1) \text{ g. of PO}_4^{3-} \text{ in 10 ml solution} \\
 \therefore \text{Strength of phosphate (PO}_4^{3-}) \text{ solution} &= 23.4 (w_2 - w_1) \text{ g. lit.}^{-1}.
 \end{aligned}$$

Experiment No. 7 : Gravimetric estimation of Cu as CuSCN

Principle :

Copper may be gravimetrically estimated by precipitating and weighing as CuSCN (solubility product = 1.99×10^{-13}). When a known volume of Cu^{2+} solution after reduction of Cu^{2+} to Cu^+ by sulphurous acid ($\text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_3$) is treated with a slight excess of potassium, or, ammonium thiocyanate solution in dilute $\sim 0.2(\text{N}) \text{H}_2\text{SO}_4$ medium, CuSCN is quantitatively precipitated.



Following conditions are to be maintained :

- The solution should be slightly acidic $\sim 0.2(\text{N})$, with respect to H_2SO_4 . Higher acidity is to be avoided as the solubility of CuSCN increases with increase of acid concentration. At much lower acidity, brown cuprous oxide, Cu_2O , tends to precipitate.
- The precipitate of CuSCN is curdy, which is coagulated by boiling.
- Precipitation should be carried out in reducing atmosphere of sulphurous acid, generated *in situ* by adding Na_2SO_3 to the acidic solution containing Cu^{2+} .
- Only a slight excess of thiocyanate should be used, as large excess may increase the solubility of CuSCN due to complex formation.
- Oxidising agents should be absent.
- The wash liquid should contain 0.01 % NH_4SCN (or KSCN) solution containing a pinch of Na_2SO_3 and a few drops of dilute sulfuric acid to prevent aerial oxidation of the cuprous salt.

Chemicals and Equipment :

- (i) Ammonium or potassium thiocyanate solution: 10% aqueous solution
- (ii) Sample copper sulphate solution, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (unknown) :
25 g.lit⁻¹ in 1(N) H_2SO_4 solution.
- (iii) Sodium sulfite (Na_2SO_3)
- (iv) G-4 Sintered glass crucible.
- (v) Desiccator with silica gel drier.
- (vi) Analytical balance with calibrated weight box.
- (vii) Air oven set at 110 – 120°C.

Procedure :

- (i) Clean a G-4 sintered-glass crucible and dry it at 110° - 120°C in the air oven for one hour. Cool the crucible in a desiccator for 25 minutes and weigh the empty crucible. Repeat the process of heating, cooling and weighing until a constant weight (± 0.0002 g.) is attained.
- (ii) Take an aliquot of 10 ml of the sample copper sulfate solution into a 250 ml beaker, add a few drops of dilute (5%) NaOH solution till a permanent faint turbidity appears. Add drops of dilute 6(N) H_2SO_4 to just dissolve the turbidity finally add 5 ml of 6(N) H_2SO_4 and dilute to 150 ml to adjust acidity ~ 0.2(N). Add ~ 1-2 g of Na_2SO_3 dissolved minimum volume of water with stirring till the blue colour due to Cu^{2+} is discharged. Heat nearly to boiling, then add 15 ml of freshly prepared 10% ammonium or potassium thiocyanate solution with stirring to precipitate CuSCN quantitatively, avoiding large excess of the reagent. White precipitate of CuSCN is immediately formed. If the precipitate appears slight brown, add a few drops of 6(N) H_2SO_4 and a few drops of dilute Na_2SO_3 solution. Cover the beaker with a clock glass and allow to stand for about 20 – 30 minutes. Check the completeness of the precipitation by adding a few drops of the thiocyanate solution to the supernatant liquid. Allow to stand for about an hour.
- (iii) Filter through the previously dried and weighed G-4 sintered glass crucible. Transfer the precipitate quantitatively from the beaker to the crucible by washing with the very dilute (0.01%) solution of ammonium or potassium thiocyanate (~1ml 10% solution diluted to 100 ml) containing small amount of dissolved Na_2SO_3 using a policeman. Wash (8-10 times) and finally 3-4 times with 20% ethanol to free from SCN^- (test with FeCl_3 solution). Dry the crucible with its contents at 110° - 120°C for one hour in an air-oven, cool in a desiccator for 25 minutes and then weigh as CuSCN . Repeat the process of heating, cooling and weighing until a constant weight (± 0.0002 g) is attained.

Calculation :

$$\begin{aligned}
 \text{Weight of empty crucible} &= W_1 \text{ g.} \\
 \text{Weight of crucible + CuSCN} &= W_2 \text{ g.} \\
 \therefore \text{Weight of CuSCN} &= (W_2 - W_1) \text{ g.} \\
 \therefore 1 \text{ g. of Cu SCN} &\equiv 0.5225 \text{ g. of Cu}^{2+} \\
 \therefore (W_2 - W_1) \text{ g. of CuSCN} &\equiv 0.5225 \times (W_2 - W_1) \text{ g of Cu}^{2+} \text{ in 10 ml solution.} \\
 \therefore 1000 \text{ ml of the Cu}^{2+} \text{ solution contains}
 \end{aligned}$$

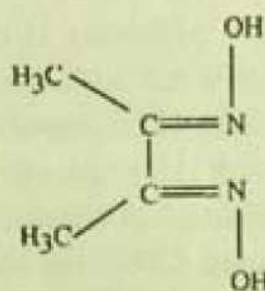
$$= \frac{0.5225 (W_2 - W_1) \times 1000}{10} \text{ g. of Cu}^{2+}$$

$$\therefore \text{Strength of Cu}^{2+} \text{ solution} = 52.25 (W_2 - W_1) \text{ g. lit}^{-1}.$$

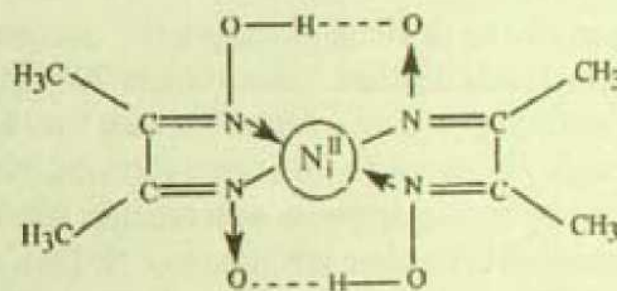
Experiment No. 8 : Gravimetric estimation of Ni as Ni(DMGH)₂

Principle :

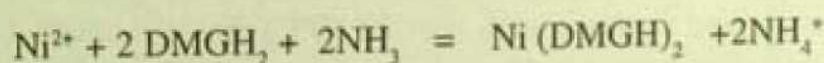
Nickel is gravimetrically estimated as *bis*-[dimethylglyoximatonickel(II)], Ni(DMGH)₂. When a known volume of Ni²⁺ solution is treated with a slight excess of ethanolic solution of dimethylglyoxime, DMGH₂ (1) in ammoniacal medium, Ni(DMGH)₂, (2) (solubility product = 3.98 × 10⁻²⁴) is quantitatively precipitated as shining red crystals.



DMGH₂
(1)



Ni^{II} (DMGH)₂
(2)



$$\therefore 288.69 \text{ g. of Ni (DMGH)}_2 \equiv 58.69 \text{ g. of Ni}^{2+}$$

$$\therefore 1 \text{ g. of Ni(DMGH)}_2 \equiv 0.2033 \text{ g. of Ni}^{2+}$$

The medium must not be acidic, since $\text{Ni}(\text{DMGH})_2$ is soluble in acid. The solution should not be strongly alkaline, as $\text{Ni}(\text{AMGH})_2$ is soluble in strong base. The optimum pH is ~ 7-8. Addition of large excess of DMGH_2 is to be avoided, as the reagent itself due to its low solubility in water may precipitate along with $\text{Ni}(\text{DMGH})_2$. Proportion of alcohol in the mixture should not be very large as the red precipitate of $\text{Ni}(\text{DMGH})_2$ may dissolve in water-alcohol mixture.

Chemicals and Equipment :

- (i) Dimethyl glyoxime solution : 1% solution in 95% ethanol .
- (ii) Ammonium nickel sulphate solution, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Ni SO}_4 \cdot 6\text{H}_2\text{O}$ (unknown): ~20.0 g.lit⁻¹ or, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ or, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ in proportional amounts in 1(N) H_2SO_4 medium.
- (iii) G-4 sintered glass crucible.
- (iv) Desiccator with silica gel drier.
- (v) Analytical balance with calibrated weight box.
- (vi) Air oven set at 110°-120°C.

Procedure :

- (i) Clean a sintered glass crucible (G - 4), and dry it at 110° - 120°C in the air oven for one hour, then cool in a desiccator for 25 minutes and weigh the empty crucible. Repeat the process of heating, cooling and weighing until a constant weight (± 0.0002 g) is attained.
- (ii) Take an aliquot of 10 ml of sample Ni^{2+} solution into a 250 ml beaker. Dilute to 150 ml with double distilled water. Heat to 70° - 80°C on a hot water bath, add 15 ml of 1% dimethyl glyoxime solution (at least 5 ml for every 10 mg of Ni present) and mix thoroughly by stirring with a clean glass rod. Neutralize with (1:1) aqueous ammonia solution by adding dropwise with constant stirring until the smell of ammonia persists and rose-red crystalline precipitate of $\text{Ni}(\text{DMGH})_2$ is formed. Cover the beaker with a clock glass and allow to stand on the hot water bath for about 20 minutes. Check the completeness of precipitation by adding a few more drops of the dimethyl glyoxime reagent solution to the supernatant liquid, smelling faintly of ammonia.
- (iii) Filter the precipitate using the previously dried and weighed sintered glass (G-4) crucible. Transfer the precipitate quantitatively from the beaker to the crucible using a policeman and washing with hot (70-80°C) distilled water. Continue washing till the filtrate is free from chloride and or sulfate (test with AgNO_3 and $\text{Ba}(\text{NO}_3)_2$ solutions in nitric acid medium). Dry the crucible with its contents at 110° - 120°C for one hour in the air-oven. Allow to cool in a desiccator for 25 minutes and then weigh. Repeat the process of heating, cooling and weighing until constant weight (± 0.0002 g.) is attained.

Calculation :

$$\begin{aligned}
 \text{Weight of empty crucible} &= W_1 \text{ g.} \\
 \text{Weight of crucible + Ni(DMGH)}_2 &= W_2 \text{ g.} \\
 \therefore \text{Weight of Ni(DMGH)}_2 &= (W_2 - W_1) \text{ g.} \\
 \because 1.0 \text{ g. of Ni(DMGH)}_2 &\equiv 0.2033 \text{ g. of Ni}^{2+} \\
 \therefore (W_2 - W_1) \text{ g. of Ni(DMGH)}_2 &\equiv 0.2033 \times (W_2 - W_1) \text{ g. of Ni}^{2+} \text{ in 10 ml solution}
 \end{aligned}$$

\therefore Strength of Ni^{2+} solution

$$= \frac{0.2033 \times (W_2 - W_1) \times 1000}{10} \text{ g.lit}^{-1}$$

$$= 20.33 (W_2 - W_1) \text{ g. lit}^{-1}.$$



Chapter – 2

Titrimetric Estimations Based on Acidimetry & Alkalimetry

Standard Substances

In titrimetric estimations, use of a standard substance is essential. The standard substances are of two types : (a) *primary standard substances* and (b) *secondary standard substances*.

A *primary standard* substance should have the following characteristics :

- The substance must be available in highly pure state (i.e., A.R. grade). It must be easy to dry (preferably at 100 – 120°C) and is preservable in the pure state.
- It should neither be hygroscopic, nor affected by air and it should not change its composition during weighing. The standard solution should be stable towards hydrolysis and photochemical decomposition during storage.
- Its equivalent weight should be reasonably high so that weighing error is minimum.
- The substance should be readily soluble in the experimental solvent medium.
- Its reaction should be rapid, quantitative and stoichiometric.

Some common primary standard substances :

<i>Alkalimetry</i>	: Anhydrous Na_2CO_3 , borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$)
<i>Acidimetry</i>	: Crystalline oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), succinic acid (CH_2COOH) ₂ , potassium hydrogenphthalate ($\text{KHC}_8\text{H}_4\text{O}_4$), potassium bi-iodate [$\text{KH}(\text{IO}_3)_2$].
<i>Oxidimetry</i>	: $\text{K}_2\text{Cr}_2\text{O}_7$, KBrO_3 , KIO_3 , $\text{KH}(\text{IO}_3)_2$.
<i>Reductimetry</i>	: Sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) etc.
<i>Complexometry</i>	: $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Some common secondary standard substances :

<i>Alkalimetry</i>	: NaOH , KOH .
<i>Acidimetry</i>	: HCl , H_2SO_4 , CH_3COOH .
<i>Oxidimetry</i>	: Potassium permanganate (KMnO_4), sodium hypochlorite.
<i>Reductimetry</i>	: Sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), Mohr's salt ($(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$)
<i>Complexometry</i>	: EDTA (Disodium salt of ethylenediamine tetraacetic acid dihydrate, $\text{Na}_2\text{H}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$).

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Depending upon chemical nature of the substances, two types of standard solutions are used in titrimetric analysis.

(a) **Primary standard solutions** : These are standard solutions of definite strength, prepared by dissolving accurately weighed quantities of the required amounts of chemically pure (A.R. grade) primary standard substances and dissolving the same in distilled water or in other specified solvents and then diluting the solutions to definite volume in volumetric flasks.

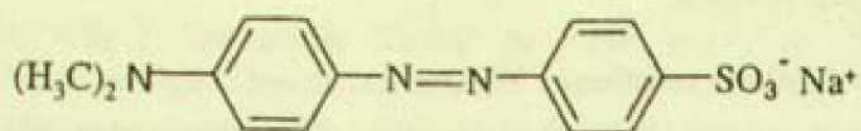
(b) **Secondary standard solutions** : These are standard solutions prepared by dissolving approximately weighed quantities of secondary standard substances in distilled water or in other specified solvents and diluting the solutions approximately to the required volume. The strengths of these solutions are determined by standardisation against some suitable primary standard solutions by titration.

Titrimetric Estimations Based on Acidimetry-Alkalimetry

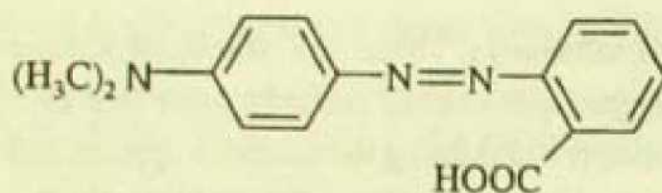
General Principle :

In quantitative estimation, the process of direct titration of an alkali by an acid is called **acidimetry**, and direct titration of an acid by an alkali is called **alkalimetry**. When an acid is titrated against an alkali solution or vice versa, it is necessary to determine the equivalence point (more precisely the end point) very accurately, with the help of an acid-base indicator. An indicator shows a characteristic colour in acidic solution and a different colour in alkaline solution. Some common acid-base indicators, their pK_{in} values and the working pH ranges are given below :

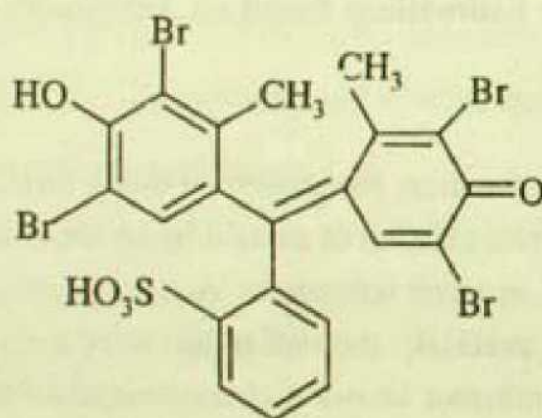
Indicator	pK_{in}	pH range	Acid colour	Alkali colour
Methyl orange	3.7	3.1 - 4.4	Red	Yellow
Bromocresol green	4.7	3.6 - 5.2	Yellow	Blue
Methyl red	5.0	4.2 - 6.3	Red	Yellow
Phenolphthalein	9.6	8.3 - 10	Colourless	Red



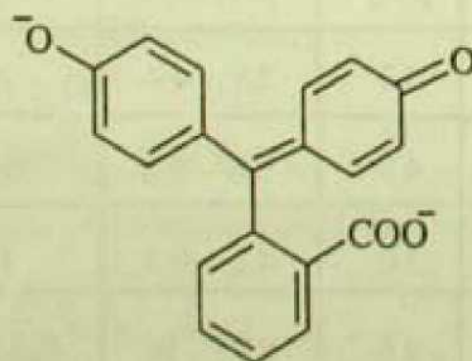
methyl orange



methyl red



bromocresol green



phenolphthalein (alkaline form)



Experiment No.1 : Preparation of ~($N/20$) of oxalic acid solution and standardisation of (i) NaOH, (ii) HCl and (iii) CH_3COOH solutions

Principle :

Oxalic acid, $\text{HOOC.COOH}, 2\text{H}_2\text{O}$ is a weak dibasic acid, so its equivalent weight as an acid = Formula weight/2 = 63.033

\therefore 1000ml (N) oxalic acid solution \equiv 63.033 g. of crystalline oxalic acid

or, 250ml ($N/20$) oxalic acid solution \equiv 0.7879 g. of crystalline oxalic acid

NaOH solution may be standardised against standard oxalic acid solution using phenolphthalein as indicator. If V_1 ml of S_1 (N) NaOH solution be required to neutralise V_2 ml of S_2 (N) oxalic acid, then

$$V_1 \times S_1 = V_2 \times S_2$$

HCl and CH_3COOH solutions may be standardised against standard NaOH solution using phenolphthalein as indicator. For HCl-NaOH titration, however, any indicator having pK_{in} value 3.5 – 9.5 may be used.

Chemicals required :

- (a) Oxalic acid (A. R.)
- (b) ~ ($N/20$) NaOH solution : 2.0 g/litre
- (c) Phenolphthalein indicator : ~0.5% in 1:1 alcohol

Procedure :

1. Preparation of standard ~($N/20$) oxalic acid solution :

Weigh out accurately about (0.7-0.8) g. (say w g.) of A.R. crystalline oxalic acid in a 250 ml volumetric flask. Add distilled water to dissolve and dilute upto the mark with distilled water and then mix uniformly. Strength = ($w / 0.7879$) ($N/20$).

2. Standardisation of NaOH solution :

Pipette out an aliquot of 25 ml of the standard ($N/20$) oxalic acid solution in a 250 ml conical flask, add 1 drop of phenolphthalein indicator. Titrate with the NaOH solution until a light pink colour appears. (See Note 1 for the Principle)

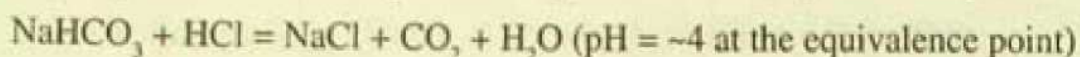
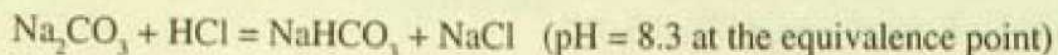
3. Standardisation of HCl/ acetic acid solution :

Pipette out an aliquot of 25ml of the supplied HCl/acetic acid solution in a 250ml conical flask, add 1 drop of phenolphthalein indicator. Titrate with the standardised NaOH solution until a light pink colour appears.

Experiment No. 2 : Estimation of NaHCO_3 and Na_2CO_3 mixture

Principle :

Neutralisation of Na_2CO_3 solution by a strong acid (HCl) occurs in two steps :



$$\therefore 1000 \text{ ml (N) HCl solution} \equiv 53 \text{ g. of } \text{Na}_2\text{CO}_3 \equiv 84 \text{ g. of } \text{NaHCO}_3$$

The acid-base indicator is to be so selected that its pH range for colour change coincides with the sudden sharp change of pH at the equivalence point. So at the first neutralisation point (pH = 8.3), phenolphthalein (pH range = 8.3-10) shows its colour change from pink to colourless. At this stage Na_2CO_3 consumes only half the amount of HCl required for complete neutralisation. If methyl orange (pH range = 3.1 to 4.4) is added to this titrated solution and the titration with HCl is continued upto the second equivalence point, then this titre value corresponds to the amount of HCl required to convert NaHCO_3 to NaCl (i.e., NaHCO_3 derived from Na_2CO_3 plus the amount of NaHCO_3 present in the original mixture).

Chemicals required :

- Standard $\sim(\text{N}/20)$ oxalic acid solution :
- $\sim(\text{N}/20)$ NaOH solution :
- $\sim(\text{N}/20)$ HCl solution:
- Phenolphthalein indicator : 0.5% solution in 1:1 aqueous ethanol
- Methyl orange : 0.05% aqueous solution
- Na_2CO_3 and NaHCO_3 mixture : Mix 35 ml (N) Na_2CO_3 solution and 15 ml (N) NaHCO_3 solution and dilute to 1litre.

Procedure :

- Standardise the (N/20) HCl solution : (See Experiment No. 1)
- Titration using phenolphthalein as indicator :

Pipette out an aliquot of 25ml from the supplied mixture in a 250ml conical flask, add 1 drop of phenolphthalein, the solution turns pink colour. Titrate the solution with the standard $\sim(\text{N}/20)$ HCl solution with constant shaking until the pink colour is just discharged. Record the titre value (V_1 ml) that corresponds to the half amount of HCl required to completely neutralise Na_2CO_3 .

3. Titration using methyl orange indicator in the same solution(a) :

Add 1-2 drops of methyl orange to the above-titrated solution when the colour of the solution turns light yellow. Titrate the solution with the same standard $\sim(N/20)$ HCl solution with constant shaking till the colour of the solution changes from yellow to red. Record the titre value (V_2 ml), which corresponds to the amount of HCl required to neutralise the remaining half amount of Na_2CO_3 (that is converted to NaHCO_3 in the first titration) and the amount of NaHCO_3 already present in the original mixture.

Calculation :

$$V_1 \equiv \frac{1}{2} (\text{Na}_2\text{CO}_3)$$

$$V_2 \equiv (\text{NaHCO}_3) + \frac{1}{2} (\text{Na}_2\text{CO}_3)$$

$$\therefore \text{NaHCO}_3 \equiv (V_2 - V_1)$$

$$\therefore \text{Na}_2\text{CO}_3 \equiv 2 V_1$$

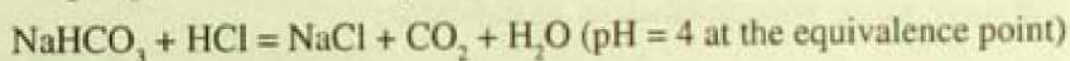
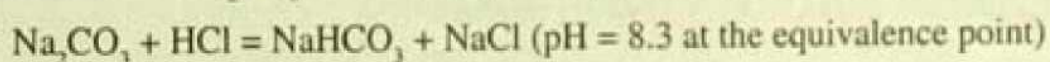
Experiment No. 3 : Estimation of Na_2CO_3 and NaOH mixture

Principle :

NaOH requires one equivalent of HCl for its neutralisation :



Neutralisation of Na_2CO_3 solution by a strong acid occurs in two steps :



$$\therefore 1000 \text{ ml (N) HCl solution} \equiv 53 \text{ gm of } \text{Na}_2\text{CO}_3 \equiv 40 \text{ gm of NaOH}$$

The acid-base indicator is to be so selected that its pH range for colour change coincides with the sudden sharp change of pH at the equivalence point (more precisely the end point). So at the first neutralisation point (pH = 8.3), phenolphthalein (pH range = 8.3-10) will show its colour change from pink to colourless. The titre value (V_1) at this stage will correspond to half of amount of HCl required for Na_2CO_3 and full amount of HCl required for NaOH. Now if methyl orange (pH range = 3.1 to 4.4) is added to the above titrated solution and the titration with HCl is continued up to the second neutralisation point, when the colour of the solution changes from yellow to red, this second titre value (V_2) will correspond to the amount of HCl required to neutralise NaHCO_3 derived from Na_2CO_3 to NaCl.

Chemicals required :

1. Standard (N/20) Na_2CO_3 solution
2. Standard \sim (N/20) HCl solution
3. Phenolphthalein indicator : 0.5% solution in 1:1 alcohol
4. Methyl orange : 0.05% aqueous solution
5. Na_2CO_3 and NaOH mixture : Mix 15ml (N) NaOH solution and 40ml (N) Na_2CO_3 solution and dilute to 1 litre.

Procedure :

1. Prepare 250 ml of (N/20) Na_2CO_3 solution. Weigh out accurately 0.6 ~ 0.8 g. of A.R. Na_2CO_3 (w g. say) into a 250 ml volumetric flask, dissolve in recently boiled and cooled distilled water, make upto the mark and mix uniformly.

Strength = $(w/0.6625)$ (N/20).

2. Standardise the (N/20) HCl solution against standard (N/20) Na_2CO_3 solution using phenolphthalein indicator.

Take an aliquot of 25 ml of the standard (N/20) Na_2CO_3 solution into a 250 ml conical flask, add one drop of phenolphthalein indicator, the solution turns pink colour. Titrate with \sim (N/20) HCl solution to a colourless end point. Calculate the strength of HCl solution using the relation

$$V_{\text{HCl}} S_{\text{HCl}} = V_{\text{Na}_2\text{CO}_3} S_{\text{Na}_2\text{CO}_3}$$

3. Estimation of $\text{Na}_2\text{CO}_3 + \text{NaOH}$ mixture.

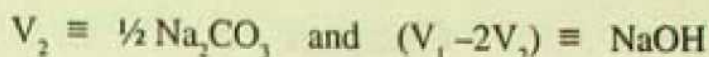
- (a) Titration using phenolphthalein as indicator :

Pipette out an aliquot of 25 ml of the supplied mixture into a 250ml conical flask, add 1-2 drop of phenolphthalein indicator, the solution turns pink colour. Titrate the solution with the standard \sim (N/20) HCl solution with constant shaking until the pink colour is just discharged. Record the titre value (V_1 ml), which corresponds to the amount of HCl required for half the amount of Na_2CO_3 and the full amount of NaOH.

- (b) Titration using methyl orange indicator in the same solution (a)

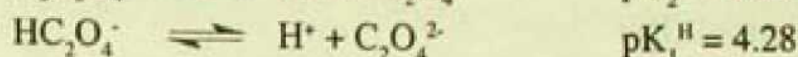
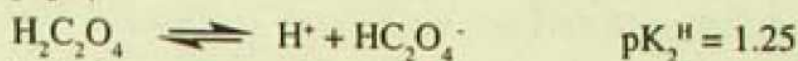
Add 1-2 drops of methyl orange to the above-titrated solution when the solution turns light yellow. Titrate the solution with the same standard \sim (N/20) HCl solution with constant shaking till the colour changes to red. Record the titre value (V_2 ml), which corresponds to remaining half amount of Na_2CO_3 .

Calculation :



Notes :

1. For oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$,



pH at the first equivalence point in the titration with NaOH is

$$\text{pH} = \frac{1}{2} (\text{pK}_2^H + \text{pK}_1^H) = \frac{1}{2} (1.25 + 4.28) = 2.77,$$

and pH at the second equivalence point of titration of N/20, i.e., (0.025 M) oxalic acid with NaOH solution will be

$$\begin{aligned} \text{pH} &= \frac{1}{2} \text{pK}_w + \frac{1}{2} \text{pK}_1^H + \frac{1}{2} \log C \\ &= 7 + \frac{1}{2} \times 4.28 + \frac{1}{2} \log (0.025) = 8.35, \quad [\text{pK}_w = 14 \text{ at } 25^\circ\text{C}] \end{aligned}$$

which is very close to the pK_{in} of phenolphthalein indicator.

2. Na_2CO_3 is a salt of strong base (NaOH) and weak acid (carbonic acid, H_2CO_3), the latter ionises in two steps :



So, pH of (N/20), i.e., (0.025 M) Na_2CO_3 solution will be

$$\begin{aligned} \text{pH} &= \frac{1}{2} \text{pK}_w + \frac{1}{2} \text{pK}_1^H + \frac{1}{2} \log C \\ &= 7 + 10.25/2 + \frac{1}{2} \log (0.025) = 11.32 \end{aligned}$$

At the first equivalence point in the titration of Na_2CO_3 with HCl, the solution will contain only the HCO_3^- as the acid-base species, which functions as an ampholyte :



The pH of such a solution will be,

$$\text{pH} = \frac{1}{2} (\text{pK}_2^H + \text{pK}_1^H) = \frac{1}{2} (6.37 + 10.25) = 8.31$$

So, phenolphthalein ($\text{pK}_{in} = 9.6$) will be the suitable indicator.

At the second equivalence point, the solution contains carbonic acid, ($\text{H}_2\text{CO}_3 \rightleftharpoons \text{CO}_2 + \text{H}_2\text{O}$), assuming no volume change and no loss of CO_2 , the pH of such a solution will be

$$\begin{aligned} \text{pH} &= \frac{1}{2} \text{pK}_2^H - \frac{1}{2} \log C \\ &= \frac{1}{2} \cdot 6.37 - \frac{1}{2} \log (0.025) = 4.0 \end{aligned}$$

This is within the pH range (3.1 – 4.4) of methyl orange. Therefore, at the point of complete neutralisation of Na_2CO_3 , the yellow colour of the solution will turn to red. This titre value of HCl will correspond to the amount of NaHCO_3 formed from Na_2CO_3 , plus the amount of NaHCO_3 present in the original mixture.

Chapter - 3

Principles of Redox Titrimetric Analyses

Electrode potential (E) :

When a metal is immersed in a solution containing its own ions (e.g., Zn in ZnSO_4 solution), a potential difference is established between the metal and the solution which is known as electrode potential or half-cell potential. The electrode potential (E) at 25°C for the system $\text{M}^{n+}(\text{aq}) + ne \rightleftharpoons \text{M}(\text{s})$ is given by Nernst equation,

$$E = E^\circ + \frac{0.059}{n} \log a_{\text{M}^{n+}(\text{aq})} \quad \dots \dots \dots (1)$$

where, $a_{\text{M}^{n+}(\text{aq})}$ = activity of $\text{M}^{n+}(\text{aq})$ and E° = standard electrode potential.

In dilute solution, the activity of $\text{M}^{n+}(\text{aq})$ is very close to its molar concentration, $[\text{M}^{n+}(\text{aq})]$, and the expression (1) for electrode potential (E) is transformed to

$$E = E^\circ + \frac{0.059}{n} \log [\text{M}^{n+}(\text{aq})] \quad \dots \dots \dots (2)$$

when $[\text{M}^{n+}(\text{aq})] = 1(\text{M})$, $E = E^\circ$ = Standard electrode potential.

Standard electrode potential (E°) :

The standard electrode potential of a redox couple may be defined as the potential obtained by combining it with a standard hydrogen electrode, SHE, (the potential of which is arbitrarily taken as zero), when all the species are present at their unit activities. Under this condition, if spontaneous reduction occurs at the electrode, then it is said to have a positive standard reduction potential (E°_{red}) and if spontaneous oxidation occurs, then it is said to have positive oxidation potential (E°_{ox}). The magnitude of the reduction potential of any electrode is equal to the oxidation potential of the same electrode with the sign opposed, i.e., $E^\circ_{\text{red}} = (-) E^\circ_{\text{ox}}$. For this reason standard electrode potentials are also called *standard redox potentials*.

There are two conventions for representing the sign of electrode potentials, e.g., with the $\text{Fe}^{3+}/\text{Fe}^{2+}$ system :



The direction of a redox reaction occurring between two redox couples may be predicted by calculating e.m.f. (E°_{Cell}) of the cell produced by coupling the two half-cells. For spontaneity of a reaction, the free energy change, ΔG° , must be negative, i.e., E°_{Cell} should be (+ve), since, $\Delta G^\circ = -nFE^\circ_{\text{Cell}}$ (n and F are positive). Thus, it follows that the oxidised form of a redox couple with a higher E°_{red} value will oxidise the reduced form of a redox couple with a lower E°_{red} value to have E°_{cell} positive, so that ΔG° is negative.

Formal potentials (E°') :

The formal potential (E°') of an electrode or a half cell is the experimentally determined potential of the cell formed by coupling a standard hydrogen electrode with the half cell having unit formal concentrations of the oxidised and the reduced forms along with those of any other species which accompany the oxidised and the reduced species under the actual reaction condition. Formal potential takes into account of the effects of hydrolysis, the pH of the solution, effects of complex formation, precipitation etc. on the stoichiometric formal concentrations of the oxidised and reduced forms appearing on the Nernst equation in dilute solution. If E°' is the formal potential at unit formal concentration of the oxidised (Ox) and the reduced (Red) forms of the redox couple,



then at 25°C, the Nernst eqn. (2) takes the form :

$$E = E^\circ + \frac{0.059}{n} \log_{10} \frac{[\text{Ox (aq)}]}{[\text{Red (aq)}]} \quad \dots\dots\dots (3)$$

If α and β be the fractions of the stoichiometric formal concentrations of the oxidised and the reduced forms respectively, i.e.,

$$[\text{Ox(aq)}] = \alpha \cdot [\text{Ox}]$$

$$[\text{Red (aq)}] = \beta [\text{Red}],$$

where, $[\text{Ox}]$ and $[\text{Red}]$ represents stoichiometric molar concentrations of Ox and Red respectively, then the eqn. (3) is transformed to,

$$E = E^\circ + \frac{0.059}{n} \log_{10} \frac{\alpha[\text{Ox}]}{\beta[\text{Red}]} \quad \dots\dots\dots (4)$$

$$\begin{aligned} &= \left(E^\circ + \frac{0.059}{n} \log_{10} \frac{\alpha}{\beta} \right) + \frac{0.059}{n} \log_{10} \frac{[\text{Ox}]}{[\text{Red}]} \\ &= E^\circ' + \frac{0.059}{n} \log_{10} \frac{[\text{Ox}]}{[\text{Red}]} \quad \dots\dots\dots (5) \end{aligned}$$

where, $E^{\circ'}$ = formal potential

$$= E^{\circ} + \frac{0.059}{n} \log_{10} \frac{\alpha}{\beta}$$

When $[Ox] = [Red]$, $E = E^{\circ'}$. The magnitude of α and β and hence that of $E^{\circ'}$ depend upon the actual composition of the reaction mixture.

Difference between standard potentials (E°) and formal potentials ($E^{\circ'}$) :

Standard potentials (E°) are of theoretical significance and are limited to the ideal systems only, i.e., when the activities of the specie are unity and the ions are present in their simple aquated forms. The values of E° are rarely observed in potentiometric measurements. On the other hand, formal potentials ($E^{\circ'}$) have practical significance as these cover the effects of activity coefficient, complex formation, precipitation, variation of pH of the solution etc. on the stoichiometric formal concentrations of the oxidised and the reduced forms. The observed potentials measured potentiometrically are the formal potentials. Some examples of variation of formal potentials are given below :

- (i) For the $Fe^{3+} + e \rightleftharpoons Fe^{2+}$ system, the standard reduction potential, $E^{\circ} = +0.77$ volt, but the formal potential, ($E^{\circ'}$) values are different in different medium :

Medium	: 1(M)HClO ₄	1(M)HCl	1(M)H ₂ SO ₄	[0.5(M)H ₂ SO ₄ + 1(M) H ₃ PO ₄]
$E^{\circ'}$ (volt)	: 0.73	0.70	0.68	0.52

This is due to the difference in the molar concentration of Fe^{3+} (aq) and Fe^{2+} (aq) from their stoichiometric concentrations, because of the different extent of complex formation / hydrolysis of these ions in different acid media.

- (ii) $E^{\circ}_{Cu^{2+}/Cu^{+}}$ is 0.15 volt, but in the presence of KI, the formal potential ($E^{\circ'}$) becomes ~0.858 volt, which is higher than the E° of the $I_2 + 2e \rightleftharpoons 2I^{-}$ system (0.54 volt). Due to precipitation of sparingly soluble cuprous iodide (Cu_2I_2), the concentration of Cu^{+} ion decreases appreciably and as a result, the formal potential increases.

Variation of redox potential during a redox titration :

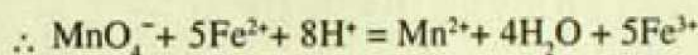
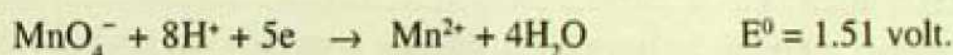
During a redox titration, there occurs a gradual change of potential of the redox couple being titrated as the proportion of the oxidant and the reductant in the system changes continuously. In the titration of 100 ml 0.1 (N) ferrous ion with 0.1 (N) permanganate solution

in $[0.5 \text{ M H}_2\text{SO}_4 + 1 \text{ M H}_3\text{PO}_4]$ medium, the potentials at different stages may be calculated as follows. The formal potential of $\text{Fe}^{3+}/\text{Fe}^{2+}$ system is lowered from $+0.77 \text{ v}$ to $+0.52 \text{ v}$, due to complex formation of Fe^{3+} with H_3PO_4 . Fe^{2+} complex with H_3PO_4 is much less stable than the Fe^{3+} complex.

$$\frac{K_{\text{Fe}^{III}(\text{HPO}_4)^+}}{K_{\text{Fe}^{III}(\text{HPO}_4)}} \geq 10^{4.2}$$

$$\begin{aligned} \therefore E^{\circ'}(\text{Fe}^{3+}/\text{Fe}^{2+}) &= E^{\circ}(\text{Fe}^{3+}/\text{Fe}^{2+}) + 0.059 \log \frac{K_{\text{Fe}^{II}(\text{HPO}_4)}}{K_{\text{Fe}^{III}(\text{HPO}_4)^+}} \\ &= +0.77 + 0.059 \log 10^{-4.2} \\ &\equiv +0.52 \text{ volt.} \end{aligned}$$

MnO_4^- oxidises Fe^{2+} to Fe^{3+} quantitatively :



(a) When 10 ml 0.1 (N) KMnO_4 is added :

$$10 \text{ ml } 0.1(\text{N}) \text{ KMnO}_4 \text{ solution} \equiv 10 \text{ ml } 0.1(\text{N}) \text{ Fe}^{2+} \text{ solution}$$

$$\equiv 10 \text{ ml } 0.1(\text{N}) \text{ Fe}^{3+} \text{ solution}$$

$$[\text{Fe}^{3+}] = (10 \times 0.1)/110 = 0.0009 \text{ (M)}$$

$$\therefore [\text{Fe}^{2+}] = (90 \times 0.1)/110 = 0.082 \text{ (M)}$$

The potential of $\text{Fe}^{3+}/\text{Fe}^{2+}$ system at this stage will be,

$$E = E^{\circ} + 0.059 \log ([\text{Fe}^{3+}] / [\text{Fe}^{2+}])$$

$$= 0.52 + 0.059 \log (0.0009 / 0.082)$$

$$= 0.463 \text{ volt.}$$

(b) When 50 ml 0.1 (N) KMnO_4 is added ; $[\text{Fe}^{2+}] = [\text{Fe}^{3+}]$

The potential of $\text{Fe}^{3+}/\text{Fe}^{2+}$ system at this stage will be $E = E^{\circ'} = 0.52 \text{ volt.}$

(c) When 90 ml 0.1 (N) KMnO_4 is added:

$$\therefore [\text{Fe}^{2+}] = (10 \times 0.1)/190 = 0.0053(\text{M})$$

$$[\text{Fe}^{3+}] = (90 \times 0.1)/190 = 0.0474(\text{M})$$

The potential of $\text{Fe}^{3+}/\text{Fe}^{2+}$ system at this stage will be.

$$\begin{aligned} E &= 0.52 + 0.059 \log (0.0474 / 0.0053) \\ &= 0.576 \text{ volt.} \end{aligned}$$

(d) When 100 ml 0.1 (N) KMnO_4 is added, i.e., at the equivalence point :

since 1 mole MnO_4^- reacts completely with 5 moles of Fe^{2+} ,

$$[\text{Fe}^{2+}] = 5[\text{MnO}_4^-] \text{ and } [\text{Fe}^{3+}] = 5[\text{Mn}^{2+}].$$

As Fe^{3+} and Mn^{2+} formed in the reaction, will also be in the same ratio,

$$\text{so, } [\text{Fe}^{3+}] / [\text{Fe}^{2+}] = [\text{Mn}^{2+}] / [\text{MnO}_4^-]$$

$$\text{or, } [\text{Fe}^{3+}][\text{MnO}_4^-] / ([\text{Fe}^{2+}][\text{Mn}^{2+}]) = 1$$

If E_{eq} be the potential at the equivalence point, then for both the systems, $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $[\text{MnO}_4^-]/[\text{Mn}^{2+}]$,

$$E_{\text{eq}} = E^\circ_{(\text{Fe}^{3+}/\text{Fe}^{2+})} + 0.059 \log ([\text{Fe}^{3+}] / [\text{Fe}^{2+}]) \dots \dots \dots (7)$$

$$\text{and } E_{\text{eq}} = E^\circ_{(\text{MnO}_4^-/\text{Mn}^{2+})} + (0.059/5) \log ([\text{MnO}_4^-][\text{H}^+]^8/[\text{Mn}^{2+}]) \dots (7a)$$

$$= E^\circ_{(\text{MnO}_4^-/\text{Mn}^{2+})} + (0.059/5) \log ([\text{MnO}_4^-] / [\text{Mn}^{2+}])$$

$$(\text{since, } [\text{H}^+] = 1\text{M})$$

$$\text{or, } 5E_{\text{eq}} = 5 E^\circ_{(\text{MnO}_4^- / \text{Mn}^{2+})} + 0.059 \log ([\text{MnO}_4^-]/[\text{Mn}^{2+}]) \dots \dots \dots (8)$$

Adding (7) & (8) one obtains,

$$6E_{\text{eq}} = 0.52 + (5 \times 1.51) + 0.059 \log ([\text{Fe}^{3+}][\text{MnO}_4^-]) / ([\text{Fe}^{2+}][\text{Mn}^{2+}])$$

$$\therefore E_{\text{eq}} = +1.345 \text{ volt.}$$

$$(\text{since, } [\text{Fe}^{3+}][\text{MnO}_4^-] / [\text{Fe}^{2+}][\text{Mn}^{2+}] = 1)$$

(e) When 100.1 ml 0.1 (N) KMnO_4 is added, the redox couple present in the solution is the $\text{MnO}_4^- / \text{Mn}^{2+}$ system. Hence the potential will be given by :

$$E = E^\circ_{(\text{MnO}_4^-/\text{Mn}^{2+})} + (0.059/5) \log ([\text{MnO}_4^-][\text{H}^+]^8/[\text{Mn}^{2+}])$$

$$= 1.51 + (0.059/5) \log [0.1 / 100] \quad (\text{since, } [\text{H}^+] = 1\text{M})$$

$$= + 1.47 \text{ volt}$$

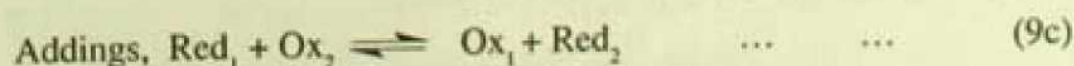
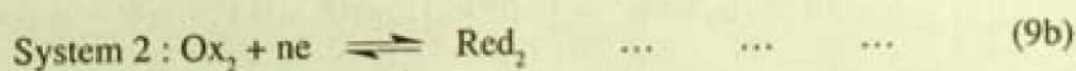
The titration data is presented in tabular form below :

Volume of KMnO_4 solution added (ml)	$[\text{Fe}^{3+}] / [\text{Fe}^{2+}]$	$[\text{MnO}_4^-] / [\text{Mn}^{2+}]$	Potential E.(volt)
10	10 : 90		0.46
50	50:50		0.52
90	90:10		0.58
99	99:1		0.64
99.9	99.9:0.1		0.70
100.0	1:1	1:1	1.35
100.1		0.1:100	1.47
101		1:100	1.49
110		10:100	1.50

A redox titration curve may be obtained by plotting the potential (E) of the solution against the volume of the oxidant (KMnO_4) added at different stages. A sharp rise in the potential is observed in the neighbourhood of the equivalence point as the redox couple active in the solution before the equivalence point is $\text{Fe}^{3+}/\text{Fe}^{2+}$ ($E^\circ = + 0.52 \text{ v}$) and after the equivalence point it is $\text{MnO}_4^-/\text{Mn}^{2+}$ ($E^\circ = 1.51 \text{ v}$).

Redox potential at the equivalence point :

At the equivalence point for a quantitatively "complete" redox titration, the two redox systems involved in the redox reaction must have a minimum limiting difference between their E° values. In the simplest case, the half-cell reactions for two reacting redox systems may be expressed according to :



The equilibrium constant, K_{eq} , is given by

$$K_{\text{eq}} = ([\text{Red}_2][\text{Ox}_1]) / ([\text{Ox}_2][\text{Red}_1]) \quad \dots \quad \dots \quad (9d)$$

At equilibrium, the electrode potentials of the two half-cells will be equal ($E_1 = E_2$). The reduction potentials of the two systems in terms of equilibrium concentrations at 25°C will be,

$$E_1 = E_1^\circ + (0.059/n) \log ([Ox_1]/[Red_1])$$

$$E_2 = E_2^\circ + (0.059/n) \log ([Ox_2]/[Red_2])$$

Since $E_1 = E_2$ at equilibrium,

$$E_2^\circ - E_1^\circ = \frac{0.059}{n} \log \frac{[Red_2][Ox_1]}{[Ox_2][Red_1]} = \frac{0.059}{n} \log K_{eq} \quad \dots \quad (10)$$

Now, for 99.9% completion of the reaction at equilibrium, each of $[Ox_1]/[Red_1]$ and $[Red_2]/[Ox_2]$ should be ~1000 : 1.

$$K_{eq} (\text{minimum}) = \frac{[Red_2][Ox_1]}{[Ox_2][Red_1]} = 10^3 \cdot 10^3 = 10^6. \quad \dots \quad (11)$$

$$\therefore \Delta E^\circ = (E_2^\circ - E_1^\circ) (\text{minimum}) = (0.059/n) \log 10^6 = (0.354/n) \text{ volt.}$$

Fe^{III} cannot be quantitatively estimated iodimetrically with high accuracy. From the E° values of Fe^{3+}/Fe^{2+} (+ 0.77 v) and I_2/I^- (+ 0.53 v) systems, the equilibrium constant K_{eq} (at 25°C) for the reaction,



may be calculated as follows :

$$\log K_{eq} = (0.77 - 0.53)/0.059 = 4.0678 \quad \therefore K_{eq} = 10^{4.07} < 10^6$$

So, at equilibrium, a small but significant amount of Fe^{3+} will remain unreacted. The minimum potential difference ($E_2^\circ - E_1^\circ$) required for a value of 10^6 for K_{eq} for the reaction between two redox couples each involving n electron(s) will be given by

$$E_2^\circ - E_1^\circ = (0.059/n) \log K_{eq} = (0.059/n) \times 6. \quad \dots \quad (12)$$

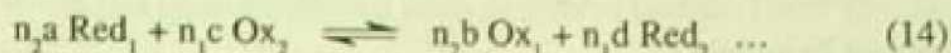
For a system with $n = 2$,

$$\Delta E^\circ = E_2^\circ - E_1^\circ = (0.059/2) \log 10^6 = 0.177 \text{ volt} = 0.2 \text{ volt} \dots \quad (13)$$

For a general case involving two redox systems :



The overall redox reaction will be



Proceeding as before one obtains :

$$\log K_{eq} = \frac{E_2^0 - E_1^0}{0.059/n_1 n_2} \dots \dots \dots (15)$$

Equivalent weights of some oxidants and reductants :

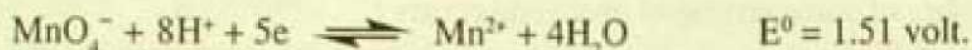
The equivalent weight of an oxidant or a reductant may be defined as the formula weight of the oxidant or reductant divided by the number of electrons gained or lost by a molecule or an ion, that is, formula weight of oxidant or reductant divided by the change of oxidation number per molecule or ion. Equivalent weights of some commonly used oxidants and reductants are summarised in the following table.

Oxidants	Nature of standard	Formula weight	Half cell reaction	Equivalent weight	Amount (g) required to prepare 250 ml (N/20) solution
K ₂ Cr ₂ O ₇	Primary	294.18	Cr ₂ O ₇ ²⁻ + 14H ⁺ + 6e ⇌ 2Cr ³⁺ + 7 H ₂ O (acid medium)	294.18/6 = 49.03	0.6129
KMnO ₄	Secondary	158.034	MnO ₄ ⁻ + 8H ⁺ + 5e ⇌ Mn ²⁺ + 4H ₂ O (acid medium)	158.034 / 5 = 31.6068	~ 0.4
			MnO ₄ ⁻ + 2 H ₂ O + 3e ⇌ MnO ₂ + 4OH ⁻ (neutral medium)	158.034 / 3 = 52.678	~ (0.6-0.7)
			MnO ₄ ⁻ + e ⇌ MnO ₄ ²⁻ (strongly alkaline medium)	158.034	~ 2
KBrO ₃	Primary	167.001	BrO ₃ ⁻ + 6H ⁺ + 6e ⇌ Br ⁻ + 3H ₂ O	167.001/6 = 27.8335	0.3479
Reductants					
Oxalic acid, H ₂ C ₂ O ₄ ·2H ₂ O	Primary	126.066	C ₂ O ₄ ²⁻ - 2e ⇌ 2CO ₂	126.066/2 = 63.033	0.7879
Na ₂ C ₂ O ₄	Primary	133.999	C ₂ O ₄ ²⁻ - 2e ⇌ 2CO ₂	133.999/2 = 66.9995	0.8375
Na ₂ S ₂ O ₃ ·5H ₂ O	Secondary	248.186	2 S ₂ O ₃ ²⁻ - 2e ⇌ S ₄ O ₆ ²⁻	248.186	~ 3-4
Mohr's salt (NH ₄) ₂ SO ₄ ·FeSO ₄ ·6H ₂ O	Secondary	392.143	Fe ²⁺ - e ⇌ Fe ³⁺	392.143	~ 5

(a) Permanganometry

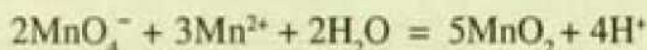
General Principle :

Permanganometry is the titrimetric analysis using a standard solution of potassium permanganate (KMnO_4) as the titrant. KMnO_4 is a strong oxidant. Its redox potential in acid medium ($\text{pH}=0$) is very high :



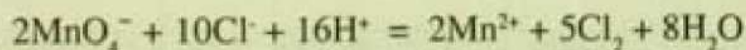
When the $\text{MnO}_4^-/\text{Mn}^{2+}$ half cell is coupled with other suitable half-cells, large ΔE^0 values results, consequently equilibrium constants ($\log K_{298} = 16.92 n \Delta E^0$, i.e., $K_{298} = 10^{16.92 n \Delta E^0}$) of the corresponding redox reactions are also very large, making these reactions virtually unidirectional and quantitative. Redox titrations are possible when the redox reaction is very rapid. Incidentally the rates of reactions of potassium permanganate are not always rapid. Rate may be increased – (i) by raising the temperature, (ii) by adding catalyst and (iii) by altering the pH of the medium.

The pink colour of very slight excess (~ one drop) of potassium permanganate solution imparts a pink colour to the titrated solution. This makes possible the detection of end point and thus KMnO_4 serves as a *self indicator*. (0.01- 0.02 ml 0.1 (N) KMnO_4 solution imparts a perceptible pink colour to 100 ml of water). The permanganate end point is not permanent because excess MnO_4^- ions react slowly with the relatively large concentration of Mn^{2+} ions present at the end point precipitating MnO_2 :



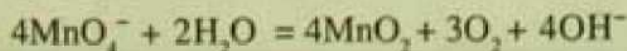
The value of the equilibrium constant for this reaction is very high, $\sim 10^{47}$, which indicates that the equilibrium concentration of MnO_4^- ion is vanishingly small even in strongly acidic medium. Fortunately, the rate of approach of this equilibrium is so slow that the end point fades only gradually over a period of ~30 seconds and so its detection is possible.

Dilute sulphuric acid medium is most suitable for permanganate titration. In dilute HCl medium, permanganate oxidises chloride to liberate chlorine :



since, $E^0 (\text{MnO}_4^- / \text{Mn}^{2+}) = 1.51 \text{ volt.}$ is much higher than $E^0 (1/2 \text{Cl}_2 / \text{Cl}^-) = 1.36 \text{ volt.}$

Potassium permanganate is not a primary standard substance, since it can not be obtained in pure state and completely free from MnO_2 . More over, ordinary distilled water is likely to contain reducing organic matters, which may tend to reduce KMnO_4 to MnO_2 and the latter catalyses the auto decomposition of MnO_4^- ion:



Bright sunlight also photochemically decomposes KMnO_4 solution. Hence, neutral aqueous solution of KMnO_4 is to be preserved in dark coloured glass stoppered bottles. There should not be any precipitate of MnO_2 .

Preparation of ~($\text{N}/20$) potassium permanganate solution :

In permanganometry, titrations are done in dilute sulfuric acid medium. So the equivalent weight of KMnO_4 corresponds to the half cell reaction,



$$1000 \text{ ml (N) } \text{KMnO}_4 \equiv (\text{KMnO}_4 / 5) \equiv (158.034 / 5) \text{ KMnO}_4 \equiv 31.60689 \text{ g. of } \text{KMnO}_4$$

Thus, in acid medium the equivalent weight of KMnO_4 is one-fifth of its formula weight. Usually ($\text{N}/10$) or ($\text{N}/20$) solution of KMnO_4 is prepared as secondary standard by dissolving ~3.2 g (or, ~ 1.6 g.) of solid KMnO_4 in 500 ml distilled water in a 1- litre beaker, gently boiled for about 15 minutes and then allowed to cool to room temperature. It is then filtered through a funnel containing a plug of glass wool to free it from MnO_2 , diluted to 1 litre with distilled water and the solution is stored in an amber coloured glass bottle. ($\text{N}/20$) KMnO_4 solution may also be prepared by proper dilution of the ($\text{N}/10$) solution.

Standardisation of KMnO_4 solution :

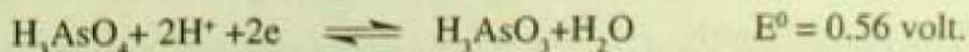
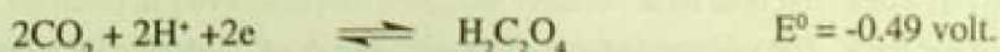
Principle :

The solution of KMnO_4 can be standardised against any one of the following three standard substances :

- (i) Crystalline oxalic acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ or sodium oxalate, $\text{Na}_2\text{C}_2\text{O}_4$
- (ii) Mohr's salt, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$
- (iii) Arsenious oxide, As_2O_3 .

The relevant half-cell reactions indicate that all the three substances are sufficiently strong reducing agents to quantitatively reduce permanganate to Mn^{2+} in acid medium.

$$E^\circ(\text{MnO}_4^- / \text{Mn}^{2+}) = 1.51 \text{ volt.}$$



When these half cells are coupled with $\text{MnO}_4^-/\text{Mn}^{2+}$ half cell, large E°_{Cell} (i.e. ΔE°) values result, and the corresponding redox reactions have high values of equilibrium constants. However, the rates of the reactions are not rapid except the one with Mohr's salt solution. The reaction rates can be increased either by raising the temperature, or by adding catalyst, or by altering the pH of the medium, as the case may be.

Cell reaction	E°_{Cell}	$K_{298} = 10^{16.92nE^\circ_{\text{Cell}}}$
$2\text{MnO}_4^- + 16\text{H}^+ + 5\text{C}_2\text{O}_4^{2-} = 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{CO}_2$	2.00 volt.	$\sim 10^{338}$
$5\text{H}_3\text{AsO}_3 + 2\text{MnO}_4^- + 6\text{H}^+ = 5\text{H}_3\text{AsO}_4 + 2\text{Mn}^{2+} + 3\text{H}_2\text{O}$	0.95 volt.	$\sim 10^{161}$
$\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ = \text{Mn}^{2+} + 4\text{H}_2\text{O} + 5\text{Fe}^{3+}$	0.74 volt.	$\sim 10^{63}$

Oxidation of oxalic acid or oxalate ion in acid medium by permanganate is slow. To initiate the oxidation, the solutions are heated to 70° to 80°C . This is further necessary to decompose the purple red complex ion, $[\text{Mn}^{\text{III}}(\text{C}_2\text{O}_4)_3]^{3-}$, formed due to local excess of KMnO_4 during titration. The complex is unstable above 60°C . Mn^{2+} ion subsequently formed, catalyses the reaction (*autocatalysis*).

Rate of oxidation of arsenious oxide by permanganate in acid medium may be increased by adding of small amount of iodide or iodate ion as catalyst.

Preparation of 250 ml $\sim(\text{N}/20)$ oxalic acid solution :

The equivalent weight of oxalic acid is half of the formula weight (126.066) of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ i.e. 63.033. For preparing 250 ml (N/20) oxalic acid solution, ~ 0.7879 g (w) of (A.R.) crystalline oxalic acid is weighed out accurately and dissolved in distilled water in a 250 ml volumetric flask. The volume is made up to the mark and shaken thoroughly to mix uniformly.

\therefore The strength of the solution will be $= (\text{w}/0.7879) (\text{N}/20) = (\text{w}/15.758) (\text{N})$

Preparation of 250 ml $\sim(\text{N}/20)$ sodium oxalate solution :

Equivalent weight of sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) is half of its formula weight (134/2) i.e. 67.0. Analytical grade sodium oxalate is to be dried at $105 - 110^\circ\text{C}$ for two hours and then cooled in a desiccator. For preparing 250 ml primary standard (N/20) solution, ~ 0.8375 g (w) of the salt is to be accurately weighed and dissolved in distilled water in a 250 ml volumetric flask. The volume is then made up to the mark with distilled water and shaken thoroughly to mix uniformly.

\therefore The strength of the solution will be $= (\text{w}/0.8375) (\text{N}/20) = (\text{w}/16.75) (\text{N})$

Preparation of 250 ml ~ (N/20) Mohr's salt solution :

Equivalent weight of Mohr's salt, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ is its formula weight, i.e., 392.143. For preparing 250 ml (N/20) solution, 4.9018 g. (w) of A.R. Mohr's salt is weighed accurately in a 250 ml volumetric flask, dissolved in previously prepared and cooled 2(N) sulphuric acid solution and the volume is made up to the mark with the same acid and mixed uniformly.

\therefore The strength of the solution will be $= (w/4.9018) (N/20) = (w/98.036) (N)$

Preparation of 250 ml ~ (N/20) arsenious oxide solution :

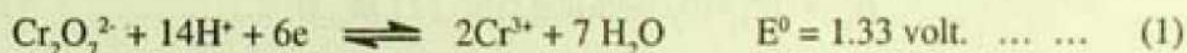
Equivalent weight of arsenious oxide, As_2O_3 , is one fourth of its formula weight (197.8412/4) i.e. 49.4603. A.R. arsenious oxide (**Caution, toxic**) is dried at $105^\circ - 110^\circ\text{C}$ for 1- 2 hours in a covered container and cooled in a desiccator. For preparing 250 ml of (N/20) solution, 0.6183 g (w) of (A.R) arsenious oxide is weighed out accurately and transferred in to a 250 ml volumetric flask by washing with 50 ml of cold 20% sodium hydroxide solution in portions. The mixture is shaken to dissolve the solid As_2O_3 completely and the volume is made up to the mark with distilled water. The solution is mixed uniformly and is allowed to stand for some time before use. (*caution: sodium arsenite solution is highly poisonous*).

\therefore The strength of the solution will be $(w/0.6183) (N/20) = (w/12.366) (N)$

(b) Dichromatometry

General Principle :

Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, acts as a strong oxidant in acid medium.



But it is a weaker oxidant than KMnO_4 ($E^0 = 1.51$ volt). When the above half cell is coupled with other suitable half-cell(s), large ΔE^0 values are often produced, giving high values of the equilibrium constants (K), making the reaction virtually unidirectional and quantitative.

The advantages of using $\text{K}_2\text{Cr}_2\text{O}_7$ over KMnO_4 are many.

- (i) $\text{K}_2\text{Cr}_2\text{O}_7$ is a primary standard substance but KMnO_4 is not a primary standard,
- (ii) It is obtained in highly pure state,

- (iii) It is very stable,
- (iv) It is highly soluble in water and its aqueous solution is stable indefinitely,
- (v) It is not reduced by cold dilute HCl, provided its strength does not exceed ~2(N),
- (vi) Solutions of $K_2Cr_2O_7$ are also less easily reduced by organic matters compared to permanganate solutions.

Using Nernst equation, the reduction potential for $Cr_2O_7^{2-}/2Cr^{3+}$ system (1) at $25^\circ C$ in dilute solution can be expressed as,

$$E = E^\circ + (0.059/6) \log \{ [Cr_2O_7^{2-}] \times [H^+]^{14} / [Cr^{3+}]^2 \} \dots \dots \dots (1a)$$

$$= (E^\circ - 0.1377pH) + (0.059/6) \log [Cr_2O_7^{2-}] / [Cr^{3+}]^2$$

$$= E^{\circ'} + (0.059/6) \log [Cr_2O_7^{2-}] / [Cr^{3+}]^2 \dots \dots \dots (1b)$$

where, $E^{\circ'} = (E^\circ - 0.1377 pH)$ is the formal potential of $Cr_2O_7^{2-}/2Cr^{3+}$ system. When the ratio $[Cr_2O_7^{2-}] / [Cr^{3+}]^2$ is 1 and $pH = 0$, $E^\circ = E^{\circ'} = 1.33$ volt., $Cr_2O_7^{2-}$ acts as a strong oxidant. But at $pH > 7$, $E^{\circ'}$ becomes < 0.366 volt., and the system can no longer act as an oxidant.

Redox Indicators :

Redox indicators are organic or inorganic redox couples having different colours in their oxidized (In_{ox}) and reduced (In_{red}) forms. Indicators show colour changes when the reduction potential of the experimental redox couple exceeds the reversible potential (E°_{In}) of the indicator couple (2),



for which, the Nerust equitation in dilute solution at $25^\circ C$ may be written as,

$$E_{In} = E^\circ_{In} + (0.059/n) \log ([In_{ox}] / [In_{red}]) \dots \dots \dots (2a)$$

Human eye can detect the colour of one form of an indicator if its concentration is 10 times that of the other form, i.e., when,

$$[In_{red}] = 10[In_{ox}] \quad E_{In} = E^\circ_{In} - 0.059/n \quad In_{red} \text{ colour prevails.}$$

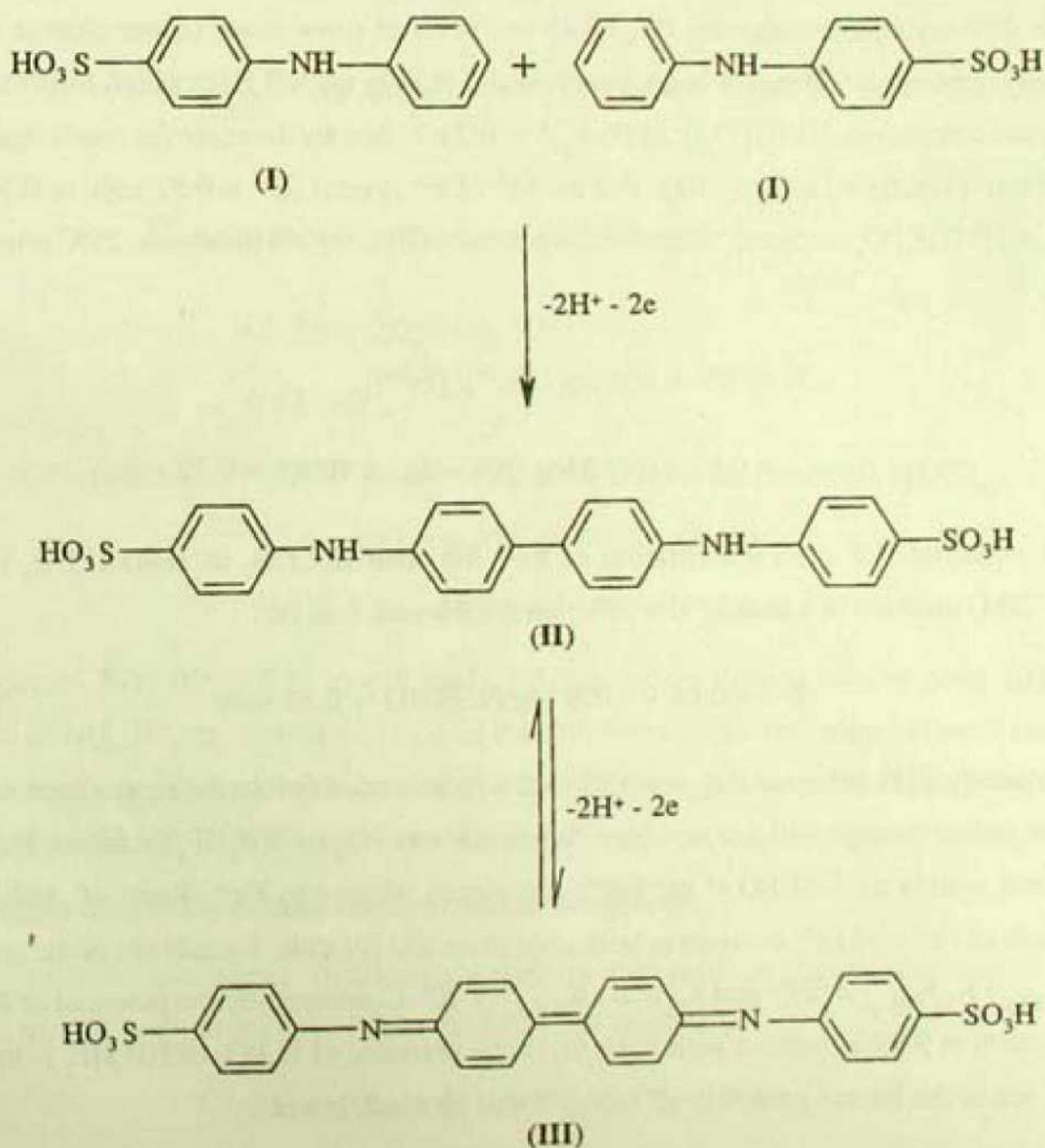
$$[In_{ox}] = 10[In_{red}] \quad E_{In} = E^\circ_{In} + 0.059/n \quad In_{ox} \text{ colour prevails.}$$

Thus, the *potential range (colour change interval)* of a redox indicator at $25^\circ C$ is,

$$E_{In} = (E^\circ_{In} \pm 0.059/n) \text{ volt.} \dots \dots \dots (2b)$$

Choice of redox indicators : A good redox indicator should show sharp colour change in the immediate vicinity of the equivalence point and its E°_{in} value should be as close as possible to the redox potential (E°_{eq}) at the equivalence point, which is somewhere intermediate between the E° values of the two redox couples involved in the redox titration. That is, the potential at the equivalence point should fall within the potential range or, colour change interval ($E^{\circ}_{in} \pm 0.059/n$) of the indicator.

Sodium /Barium diphenylaminesulphonate (I), (BDS), is a commonly used redox indicator in dichromatometry. In acid solution it is irreversibly oxidised by air to the colourless bis-(4-sulphonatophenyl) benzidine (II) which acts as the real indicator. (II) is reversibly oxidised to deep violet bis-(4-sulphonatophenyl) benzidine violet (III).



In case of barium diphenylaminesulphonate (BDS) indicator ($E^\circ_{\text{BDS}} = +0.85$ volt, and $n = 2$), the useful potential range is (0.82 - 0.88) volt. At potentials below 0.82 volt., the reduced form of the indicator (II) predominates and the indicator solution is colourless. At potentials above 0.88 volt., the violet coloured quinonoid form (III) predominates and the colour of the solution becomes violet. On standing the oxidised indicator for long time, it is gradually irreversibly oxidised to colourless product of indefinite stoichiometry.

Around the equivalence point, in the titration of Fe^{2+} with $\text{K}_2\text{Cr}_2\text{O}_7$ in acid solution, the potential of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ changes from ~ 0.7 volt. (at 99.9% titration) to ~ 1.47 volt. (at 100.1% titration). Potential at the equivalence point is ~ 1.35 volt. Under these circumstances, barium diphenylaminesulphonate ($E^\circ_{\text{BDS}} = 0.85$ volt) cannot show sharp colour change near the equivalence point. Hence it is necessary to add H_3PO_4 or NH_4HF_2 , which form stable colourless complexes, $[\text{Fe}(\text{HPO}_4)]^+$ or $[\text{FeF}_6]^{3-}$ with Fe^{3+} , thereby decrease the concentration of Fe^{3+} ion (say, by a factor $\geq 10^6$). For the $\text{Fe}^{3+}/\text{Fe}^{2+}$ system ($E^\circ = 0.52$ volt. in 0.5(M) H_2SO_4 + 1(M) H_3PO_4 medium), the reduction potential (E) at 99.9% titration at 25°C remains at,

$$\begin{aligned} E &= E^\circ + 0.059 \log ([\text{Fe}^{3+}]/[\text{Fe}^{2+}]) \\ &= 0.52 + 0.059 \log ([99.9/(0.1 \times 10^6)]) = 0.70 \text{ volt.} \end{aligned}$$

Redox potential (E) at 99.9% titration of Fe^{2+} ion with $\text{K}_2\text{Cr}_2\text{O}_7$ in 1(M) H_2SO_4 (i.e., $[\text{H}^+] = 2(\text{M})$ medium at which $E^\circ (\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.68$ volt, will be :

$$E = +0.68 + 0.059 \log (9.99/0.1) = 0.86 \text{ volt.}$$

Consequently BDS indicator ($E^\circ_{\text{BDS}} = +0.85$ volt) will be oxidised before the equivalence point and the colour change will not be sharp. When 85% H_3PO_4 or NH_4HF_2 is added, Fe^{3+} is stabilized mainly as $\text{Fe}(\text{HPO}_4)^+$ or, FeF_6^{3-} complexes relative to Fe^{3+} . Ratio of stability constants of Fe^{3+} and Fe^{2+} complexes with phosphate and fluoride ligands are of the order, $K_{\text{Fe}^{3+}(\text{HPO}_4)} : K_{\text{Fe}^{2+}(\text{HPO}_4)} \geq 10^{12}$ and $K_{\text{Fe}^{3+}(\text{F}_6)} : K_{\text{Fe}^{2+}(\text{F}_6)} \geq 10^9$. Consequently the potential of $\text{Fe}^{3+}/\text{Fe}^{2+}$ system at 9.99% titration with $\text{K}_2\text{Cr}_2\text{O}_7$ in the presence of H_3PO_4 or NH_4HF_2 is much lower, since, the formal potential, $E^\circ' (\text{Fe}^{3+}/\text{Fe}^{2+})$ will be much lower.

In the presence of H_2PO_4

$$K_{\text{Fe}^{3+}/\text{Fe}^{2+}} = \frac{[\text{Fe}^{3+}][\text{HPO}_4^{2-}]}{[\text{Fe}^{2+}][\text{H}_2\text{PO}_4^-]} \quad K_{\text{Fe}^{3+}/\text{Fe}^{2+}} = \frac{[\text{Fe}^{3+}][\text{HPO}_4^{2-}]}{[\text{Fe}^{2+}][\text{H}_2\text{PO}_4^-]}$$

$$\therefore \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} = \frac{[\text{Fe}^{3+}][\text{HPO}_4^{2-}] \times K_{\text{Fe}^{3+}/\text{Fe}^{2+}}}{K_{\text{Fe}^{3+}/\text{Fe}^{2+}} \times [\text{Fe}^{2+}][\text{HPO}_4^{2-}]}$$

$$\therefore E = E^{\circ}(\text{Fe}^{3+}/\text{Fe}^{2+}) + 0.059 \log \frac{K_{\text{Fe}^{3+}/\text{Fe}^{2+}}}{K_{\text{Fe}^{3+}/\text{Fe}^{2+}}} + 0.059 \log \frac{[\text{Fe}^{3+}][\text{HPO}_4^{2-}]}{[\text{Fe}^{2+}][\text{HPO}_4^{2-}]}$$

$$= E^{\circ}(\text{Fe}^{3+}/\text{Fe}^{2+}) + 0.059 \log \frac{[\text{Fe}^{3+}][\text{HPO}_4^{2-}]}{[\text{Fe}^{2+}][\text{HPO}_4^{2-}]}$$

where, $E^{\circ}(\text{Fe}^{3+}/\text{Fe}^{2+})$ is the formal potential of $\text{Fe}^{3+}/\text{Fe}^{2+}$ system under this condition, and is given by,

$$E^{\circ}(\text{Fe}^{3+}/\text{Fe}^{2+}) = E^{\circ}(\text{Fe}^{3+}/\text{Fe}^{2+}) + 0.059 \log \frac{K_{\text{Fe}^{3+}/\text{Fe}^{2+}}}{K_{\text{Fe}^{3+}/\text{Fe}^{2+}}}$$

$$= +0.68 + 0.059 \log 10^{-4.2}$$

$$= 0.43 \text{ volt.}$$

Therefore, the potential of $\text{Fe}^{3+}/\text{Fe}^{2+}$ system at 99.9% titration in the presence of H_2PO_4 will be

$$E = E^{\circ}(\text{Fe}^{3+}/\text{Fe}^{2+}) + 0.059 \log (99.9/0.1)$$

$$= 0.43 + 0.059 \log 999 = 0.61 \text{ volt.}$$

Consequently, BDS ($E^{\circ}_{\text{red}} = 0.85 \text{ v}$) will not be oxidised before the equivalence point. In the presence of NH_4HF_6 , the formal potential of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ system is further lowered, since $K_{\text{Fe}^{3+}/\text{Fe}^{2+}} : K_{\text{Fe}^{3+}/\text{Fe}^{2+}} \geq 10$. Under this condition, barium diphenylamine sulphonate (potential range 0.82 - 0.88 volt at 25°C), functions as a suitable indicator.

Preparation of -(N/20) potassium dichromate solution :

In dichromatometry, titrations are done in acid medium. Equivalent weight of $\text{K}_2\text{Cr}_2\text{O}_7$ in acid medium corresponds to the half - cell reaction :



$$\therefore 1 \text{ Equivalent of } K_2Cr_2O_7 = (K_2Cr_2O_7)/6 = 294.18/6 = 49.03$$

$$\therefore 1000 \text{ ml (N) } K_2Cr_2O_7 \text{ requires } 49.03 \text{ g. of } K_2Cr_2O_7.$$

$$\therefore 250 \text{ ml (N/20) } K_2Cr_2O_7 \text{ requires } 0.6129 \text{ g. of } K_2Cr_2O_7.$$

About 0.6–0.7(w) g of A.R. $K_2Cr_2O_7$ is weighed out accurately in a 250 ml volumetric flask, dissolved in distilled water, diluted upto the mark and mixed uniformly by shaking.

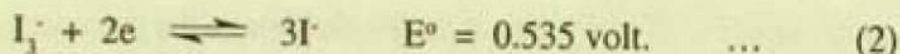
$$\therefore S (K_2Cr_2O_7) = (w / 0.6129)(N/20)$$

(c) Iodometry and Iodimetry

Iodimetry refers to the titration with a standard iodine solution while titration of liberated iodine with a standard solution of sodium thiosulfate is known as *iodometry*. Iodine (I_2) is a weak oxidant. In presence of an excess of iodide (I^-) ion, iodine is converted to the tri-iodide ion (I_3^-):

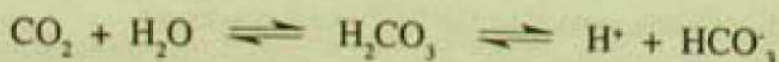


Consequently, the $I_2/2I^-$ redox couple in the presence of excess of iodide ion may be represented as

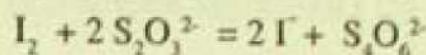


If a known amount of a strong oxidising agent such as $K_2Cr_2O_7$ is treated with an excess of iodide ion in acidic solution, iodide is quantitatively oxidised by the oxidant and an equivalent amount of iodine is liberated. The liberated iodine is titrated with a reducing agent, usually sodium thiosulfate, which quantitatively reduces iodine to iodide and it self is oxidised to sodium tetrathionate, $Na_2S_4O_6$.

Sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) is not a primary standard substance because its crystals are efflorescent, its aqueous solution is unstable and on standing turns turbid due to the separation of colloidal sulfur, which is caused by atmospheric CO_2 or by bright sunlight and by bacteria:



For these reasons, thiosulfate solution is to be standardised against a primary standard substance, such as $K_2Cr_2O_7$ or $KBrO_3$ etc. In acid medium, $Cr_2O_7^{2-}$ quantitatively oxidises I^- to I_2 and the liberated I_2 is titrated with thiosulfate solution using starch as indicator.



$$\therefore \frac{Cr_2O_7^{2-}}{6} \equiv I^- \equiv \frac{1}{2} I_2 \equiv S_2O_3^{2-}$$

\therefore 1000 ml of (N) $K_2Cr_2O_7 \equiv$ 1000 ml of (N) thiosulfate

\equiv 1000 ml of (N) iodine

If I_2 liberated by V_1 ml of S_1 (N) $K_2Cr_2O_7$ solution consumes V_2 ml of S_2 (N) thiosulfate solution, then,

$$V_1 \times S_1 = V_2 \times S_2$$

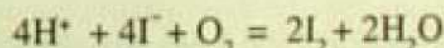
$$\text{or, } S_2 = \frac{V_1 \times S_1}{V_2} (N)$$

Notes

1. Sources of errors in iodometric titration :

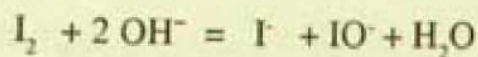
(a) Loss of iodine results due its high volatility. In the presence of an excess of iodide, the volatility of I_2 is reduced appreciably due to the formation of tri-iodide ion, $I_2 + I^- \rightleftharpoons I_3^-$. At room temperature, the loss of iodine due to volatility is negligible in the presence of ~4% excess of KI solution. If prolong standing is necessary, air inside the flask should be removed by CO_2 before adding iodide. This may be achieved by adding a small amount (0.2 – 0.5 g) of $NaHCO_3$ in acid medium. Iodometric titrations should be done as quickly as possible in the cold condition in a conical flask (not in beaker) to avoid exposure to air.

(b) Aerial oxidation of iodide : HI produced from the reaction of excess of iodide in acid medium is susceptible to aerial oxidation to iodine according to :



especially in presence of Cr^{3+} . The reaction is not instantaneous but it is catalysed by Fe^{3+} and Cu^+ ions. To prevent aerial oxidation of iodide the titration has to be carried out in CO_2 atmosphere and the flask should be kept covered as much as possible. To ensure quantitative oxidation of iodide to iodine and to avoid photochemical oxidation of iodide, the reaction mixture is to be kept in the dark for about 2-3 minutes.

2. Effect of pH : The standard reduction potential of $I_2 / 2I^-$ couple is independent of pH of the solution till the pH is less than 8. At $pH > 8$, iodine may disproportionate to hypoiodite, IO^- , and iodide (I^-). Hypoiodite readily disproportionates to iodate, IO_3^- and iodide, I^- , at still higher pH :



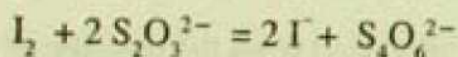
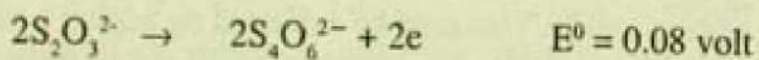
Hence iodometric titrations should always be done at a $pH < 8$.

3. For standardisation of thiosulfate, the acidity of the solution for liberation of iodine is to be maintained at $\sim 2(N)$. For titration of I_2 with thiosulfate, acidity should be lowered below $0.5 (N)$ by dilution with water. In strongly acidic medium thiosulfate is decomposed with separation of sulfur (discussed before).

4. It is advisable to use freshly prepared solution of sodium thiosulfate dissolved in recently boiled and cooled distilled water, since in aqueous solution of thiosulfate is unstable and turns turbid due to separation of colloidal sulphur on standing.

Preparation of $\sim(N/20)$ sodium thiosulfate solution:

Sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$, is readily available in a high purity state, but its exact number of water of crystallisation remains uncertain because of its efflorescent nature. Its aqueous solution gradually turns turbid on standing due to the separation of colloidal sulphur. That is why this substance is not used as a primary standard. Thiosulfate is a moderately strong reducing agent and it is widely used to determine oxidants by an indirect method that involves iodine-iodide redox couple as intermediate. The thiosulfate ion ($S_2O_3^{2-}$) is quantitatively oxidised to tetrathionate ion ($S_4O_6^{2-}$) by iodine.



$$E_{\text{cell}}^0 = (0.54 - 0.08) \text{ volt} = 0.46 \text{ volt}; \quad K_{298} = 10^{15.57}$$

In this reaction, each thiosulfate ion loses one electron. So the equivalent weight of $Na_2S_2O_3 \cdot 5H_2O$ is its formula weight (248.186). To obtain 1 litre of $\sim(N/20)$ thiosulfate solution ~ 12.5 g of A.R. $Na_2S_2O_3 \cdot 5H_2O$ may be dissolved in recently boiled and cooled distilled water and diluted to 1 litre and shaken well to mix uniformly. Thiosulfate solution is to be stored in amber-coloured bottles. 3 to 4 drops of chloroform may be added to enhance the keeping quality of the solution.

Chapter – 4

Redox Titrimetric Estimations Based on Permanganometry

Experiment No. 1 : Standardisation of KMnO_4 solution with standard sodium oxalate/oxalic acid solution :

Principle :

In dilute H_2SO_4 acid medium MnO_4^- quantitatively oxidises $\text{C}_2\text{O}_4^{2-}$ to CO_2 and itself is reduced to Mn^{2+} ,



$$\therefore \frac{\text{MnO}_4^-}{5} \equiv \frac{\text{C}_2\text{O}_4^{2-}}{2} = 1 \text{ Equivalent}$$

$$\therefore 1000 \text{ ml of (N) oxalate} \equiv 1000 \text{ ml of (N) permanganate}$$

It is an example of *autocatalytic* reaction, in which Mn^{2+} , a product of the reaction, acts as the catalyst. Use of sodium oxalate as the primary standard substance is advantageous over oxalic acid, because the former has no water of crystallisation and can be easily purified by recrystallisation. Further, its strength does not change on standing.

KMnO_4 solution may be standardised against standard oxalic acid/sodium oxalate solution in 2(N) H_2SO_4 medium at $70 \sim 80^\circ\text{C}$. Purple coloured KMnO_4 serves as a *self indicator*. Its strength may be calculated using the relation :

$$V_{\text{MnO}_4^-} \times S_{\text{MnO}_4^-} = V_{\text{C}_2\text{O}_4^{2-}} \times S_{\text{C}_2\text{O}_4^{2-}}$$

Chemicals required :

- Standard (N/20) oxalic acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (F.W. = 126.048) or Sodium Oxalate, $\text{Na}_2\text{C}_2\text{O}_4$, (F.W. = 134) to be prepared by accurate weighing.

$$\begin{aligned} \text{Strength} &= \left(\frac{w}{0.7879} \right) (\text{N/20}) \quad \text{for oxalic acid} \\ &= \left(\frac{w'}{0.8375} \right) (\text{N/20}) \quad \text{for sodium oxalate} \end{aligned}$$

where, w and w' are the weights of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ or $\text{Na}_2\text{C}_2\text{O}_4$ respectively per 250 ml of the solution.

- (~N/20) KMnO_4 solution : ~ 0.4 – 0.5 g. of KMnO_4 per 250 ml.
- 4(N) H_2SO_4 : (1 : 9) H_2SO_4 solution.

Procedure :

Pipette out an aliquot of 25 ml of (N/20) standard oxalic acid or sodium oxalate in a 250 ml conical flask, add 25 ml of 4 (N) H_2SO_4 and heat to about $70 - 80^\circ\text{C}$ and titrate the hot solution with the (\sim N/20) KMnO_4 solution until the solution turns light pink colour that is stable for \sim 30 seconds. Repeat the titration twice to have a concordant reading. Calculate the strength of KMnO_4 solution.

Experiment No. 2 : Standardisation of Mohr's salt solution / estimation of Fe^{II} with standard KMnO_4 solution

Principle :

In dilute H_2SO_4 acid medium, KMnO_4 quantitatively oxidises Fe^{2+} to Fe^{3+} :



$$\therefore \text{MnO}_4^- \equiv 5\text{Fe}^{2+}$$

$$\therefore \frac{\text{MnO}_4^-}{5} \equiv \text{Fe}^{2+} \equiv (\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$$

Mohr's salt (Fe^{2+}) solution may be estimated by titrating it, in 2(N) H_2SO_4 medium with a standard solution of KMnO_4 at room temperature in presence of H_3PO_4 .

Calculation :

$$\therefore 1000 \text{ ml of (N) } \text{KMnO}_4 \equiv 55.847 \text{ g of Fe} \equiv 392.143 \text{ g of Mohr's salt}$$

$$\text{or, } 1000 \text{ ml (N) } \text{KMnO}_4 \equiv 1000 \text{ ml (N) Mohr}$$

$$\text{i.e., } V(\text{KMnO}_4) \times S(\text{KMnO}_4) = V(\text{Mohr}) \times S(\text{Mohr})$$

Chemicals required :

- 1) Standard (M/20) oxalic acid or sodium oxalate solution : To be prepared by accurate weighing.
- 2) 4(N) H_2SO_4
- 3) Syrupy phosphoric acid
- 4) (\sim N/20) Mohr's salt solution : \sim 5 g. of Mohr's salt per 250 ml in 2(N) H_2SO_4 .

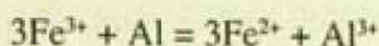
Procedure :

Pipette out an aliquot of 25 ml of Mohr's salt solution in a 250 ml conical flask, add 25 ml 4 (N) H_2SO_4 and 3 ml of syrupy H_3PO_4 and titrate the solution with the standardised (N/20) KMnO_4 solution up to a light pink colour, that is stable for 30 seconds. Repeat the titration twice to have a concordant reading. Calculate the strength of Mohr's salt solution in normality and in g.lit⁻¹.

Experiment No. 3 : Estimation of Fe^{III}

Principle :

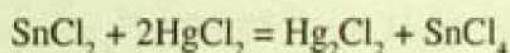
Fe^{3+} is to be first reduced to Fe^{2+} in 5-6(N) HCl medium, either by Al-foil according to,



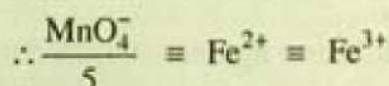
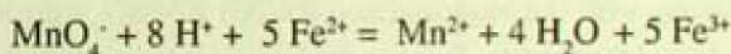
or by SnCl_2 solution according to,



SnCl_2 solution is added dropwise in hot 6(N) HCl medium till the yellow colour of the FeCl_4^- complex is discharged. One drop of SnCl_2 is to be added in excess after discharge of the yellow colour. After cooling the solution to room temperature, the excess SnCl_2 is to be consumed by adding HgCl_2 solution, when a silky white precipitate of Hg_2Cl_2 appears. This ensures the completeness of reduction of Fe^{3+} to Fe^{2+} .



KMnO_4 quantitatively oxidises Fe^{2+} to Fe^{3+} in 2(N) H_2SO_4 acid medium in presence of H_3PO_4 and itself is reduced to Mn^{2+} :

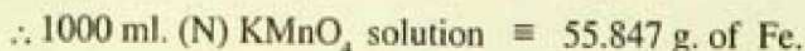
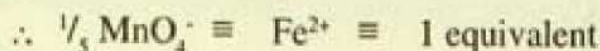


H_3PO_4 complexes Fe^{3+} in preference to Fe^{2+} and keeps the formal potential of $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple much lower than that of $\text{MnO}_4^-/\text{Mn}^{2+}$ couple. As a result, oxidation of Fe^{2+} to Fe^{3+} by MnO_4^- becomes quantitative near the equivalence point.

Usually a mixture of ($\text{H}_3\text{PO}_4 + \text{H}_2\text{SO}_4 + \text{MnSO}_4$), called *Zimmerman-Reinhardt Reagent (Z-R reagent)* is added. H_2SO_4 maintains the acidity. H_3PO_4 complexes Fe^{3+} and lowers the formal potential of $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple. MnSO_4 (i.e., Mn^{2+}) keeps the formal potential

of $\text{MnO}_4^- / \text{Mn}^{2+}$ couple at such a low value in this low acidity ($\sim 0.8\text{N}$) solution, that only Fe^{2+} is oxidised by MnO_4^- , but chloride is not oxidised (since E° of $\text{Cl}_2/2\text{Cl}^- = 1.36 \text{ v}$).

Calculation :



Chemicals required :

- 1) Standard (N/20) oxalic acid or sodium oxalate solution, to be prepared by accurate weighing.
- 2) 15% SnCl_2 solution or Al-foil.
- 3) 5%- HgCl_2 solution.
- 4) Zimmermann – Reinhardt reagent (see Appendix - A).

Procedure :

1(a). SnCl_2 reduction method :

Pipette out an aliquot of 25ml from the supplied Fe^{III} solution in a 500ml conical flask, add 18 ml conc. HCl , heat nearly to boiling and then reduce with SnCl_2 solution by adding the SnCl_2 solution dropwise with constant shaking until the yellow colour of the Fe^{III} solution is just discharged. Add one drop of SnCl_2 in excess. Cool the flask rapidly under tap water to room temperature. Add 10ml of 5% HgCl_2 solution **at a time**, shake and allow to stand for about 5 minutes, when a silky white precipitate of Hg_2Cl_2 appears. This indicates the completeness of reduction of Fe^{3+} to Fe^{2+} . Dilute the solution with 250 ml of distilled water to maintain the acidity below 0.8N, add 25 ml Zimmermann-Reinhardt solution and titrate the solution with the standardised (N/20) KMnO_4 solution upto a light pink colour, that is stable for ~ 15 seconds. Repeat the titration twice to have a concordant reading.

Standardise the ($\sim \text{N}/20$) KMnO_4 solution against standard oxalic acid/sodium oxalate as usual and find the strength of Fe^{III} solution in normality and in g.lit^{-1} .

(b) Al-foil reduction method :

Pipette out an aliquot of 25 ml of the Fe^{III} solution in a 500 ml conical flask, add 18 ml conc. HCl and a few pieces of A.R. Al-foils to the solution. Heat carefully and shake by swirling the flask till the yellow colour of the solution is discharged (add 1-2 more pieces of A.R. Al-foils if the yellow colour of the solution still persists). Note that the foils are completely disintegrated and a clear solution is produced.



Dilute the solution with 250 ml water to maintain the acidity below 0.8N, add 25 ml Zimmermann-Reinhardt solution and titrate the solution with the standardised (N/20) KMnO_4 solution upto light pink colour, that is stable for ~15 seconds. Repeat the titration twice to have a concordant reading.

Standardise the (~N/20) KMnO_4 against standard oxalic acid/sodium oxalate and find the strength of Fe^{III} solution as usual.

Experiment No. 4 : Estimation of Fe^{II} and Fe^{III} in mixture

Principle :

Direct titration of the $\text{Fe}^{\text{II}} + \text{Fe}^{\text{III}}$ mixture with standard KMnO_4 solution in $2(\text{N})\text{H}_2\text{SO}_4$ medium in presence of Zimmermann-Reinhardt reagent ($\text{H}_3\text{PO}_4 + \text{H}_2\text{SO}_4 + \text{MnSO}_4$) gives the amount of Fe^{II} . After reduction of Fe^{3+} to Fe^{2+} , if the mixture is titrated with a standard KMnO_4 solution in presence of Zimmermann-Reinhardt reagent, then this titre value will correspond to the total iron [$\text{Fe}^{2+} + \text{Fe}^{3+}$]. The difference of the titre values will give the amount of Fe^{III} . Reduction of Fe^{3+} may be effected in 5-6 (N) HCl medium either by Al-foil or by stannous chloride, (see Experiment - 3).



$$\therefore (\text{MnO}_4^- / 5) \equiv \text{Fe}$$

$$1000 \text{ ml (N) } \text{KMnO}_4 \text{ solution} \equiv 55.847 \text{ g. of Fe.}$$

Chemicals required :

1. Standard (N/20) oxalic acid or sodium oxalate solution : to be prepared by accurate weighing.
2. 15% SnCl_2 solution or, Al-foil.
3. 5% HgCl_2 solution.
4. Zimmermann-Reinhardt reagent (Z. R. Reagent) : (See Appendix - A).
5. 4(N) and 2(N) H_2SO_4 solution.

Procedure :

1. Determination of Fe^{II} :

Pipette out an aliquot of 25 ml of the ($\text{Fe}^{\text{II}} + \text{Fe}^{\text{III}}$) mixture in a 500 ml conical flask, add 25 ml 2 (N) H_2SO_4 and 25 ml. of Z. R. reagent and titrate the solution with the standardised (N/20) KMnO_4 solution until the solution turns light pink colour, that is stable for 30 seconds. Repeat the titration twice to have a concordant reading. (Titre value = V_1 ml).

(ii) Determination of total iron ($\text{Fe}^{2+} + \text{Fe}^{3+}$) :

Pipette out an aliquot of 25 ml of the ($\text{Fe}^{II} + \text{Fe}^{III}$) mixture in a 500 ml. conical flask, add 18 ml conc. HCl, heat nearly to boiling and then reduce Fe^{III} with Al-foil as usual. Alternatively reduce with SnCl_2 solution as usual (see Experiment-3). Dilute the solution with 250 ml of distilled water, add 25 ml of Z. R. reagent. Titrate the solution with the standardised (N/20) KMnO_4 solution until the solution turns light pink colour, that remains stable for ~15 seconds. Repeat the titration twice to have a concordant reading. (Titre value = V_2 ml).

(iii) Standardise the (~N/20) KMnO_4 solution against standard (N/20) oxalic acid / sodium oxate following the usual procedure (see Experiment-1).

Calculation :

$$S(\text{MnO}_4^-) = \frac{V(\text{C}_2\text{O}_4^{2-}) \cdot S(\text{C}_2\text{O}_4^{2-})}{V(\text{MnO}_4^-)}$$

$$1000 \text{ ml of (N) } \text{KMnO}_4 \equiv \text{Fe} \equiv 55.847 \text{ g. of Fe.}$$

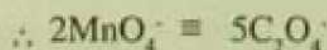
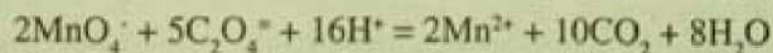
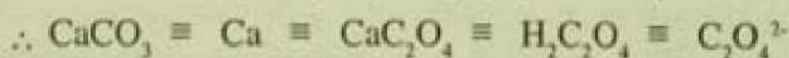
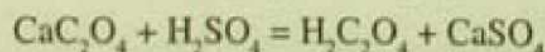
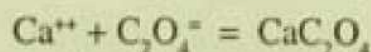
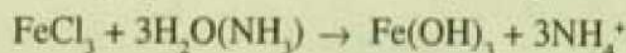
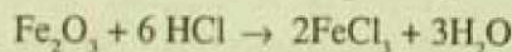
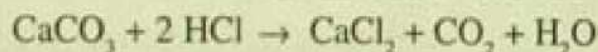
$$V_1 \text{ ml standard (N/20) } \text{KMnO}_4 \equiv \text{Fe}^{II}$$

$$(V_2 - V_1) \text{ ml standard (N/20) } \text{KMnO}_4 \equiv \text{Fe}^{III}$$

Experiment No. 5 : Estimation of CaCO_3 in dolomite

Principle :

Dolomite ore contains CaCO_3 and MgCO_3 as major components and SiO_2 and Fe_2O_3 as trace constituents. A known weight of finely ground dolomite is dissolved in 1:1 HCl by gentle heating. From the solution Fe^{3+} is first separated by precipitating as ferric hydroxide, Ca^{2+} is then precipitated from the filtrate as calcium oxalate (CaC_2O_4), which is filtered and washed free from adhering chloride and oxalate ions and then dissolved in hot dil. H_2SO_4 , when an equivalent amount of oxalic acid liberated, which is then titrated with standard KMnO_4 solution to obtain the amount of Ca, hence CaCO_3 .



$$\therefore \frac{\text{MnO}_4^-}{5} = \frac{\text{C}_2\text{O}_4^{2-}}{2} = \frac{\text{Ca}}{2} = \frac{\text{CaCO}_3}{2} = \frac{40.08}{2} \text{ g. of Ca} = \frac{100.08}{2} \text{ g. of CaCO}_3$$

$$\therefore 1000 \text{ ml (N) KMnO}_4 \text{ solution} \equiv 20.04 \text{ g of Ca.} \equiv 50.04 \text{ g. CaCO}_3$$

Chemicals required :

- 1) Standard (N/20) oxalic acid/sodium oxalate to be prepared by accurate weighing.
- 2) 4% Ammonium oxalate solution.
- 3) 4(N) H_2SO_4 , conc. HCl , conc. HNO_3 (all A.R.).
- 4) (1 : 1) Aqueous – ammonia.
- 5) Methyl red indicator.
- 6) Whatman No. 40 & 42 filter papers.

Procedure :

1. Dissolution of Dolomite :

Attack ~1.0 g of finely powdered ore with 10 ml of water, 5 ml conc. HCl and 1 ml conc. HNO_3 in a 250 ml beaker and heat gently on an asbestos board till dissolution. Evaporate the solution almost to dryness, cool, and then moisten the residue with 2-3 ml of conc. HCl , and evaporate nearly to dryness. Repeat this operation twice and then bake the residue for 5 minutes, cool, and add 50 ml of (1 : 6) HCl and heat to boiling, when all the soluble salts are dissolved. Cool to room temperature and filter the solution through a Whatman No. 40 filter paper into a 250ml volumetric flask and make up the volume to 250ml with distilled water.

2. Estimation of Ca^{2+} :

Pipette out 25 ml. of the stock solution in a 500 ml beaker, dilute to about 200 ml and add a few drops of methyl red indicator, neutralise with 1:1 aqueous ammonia to a just yellow colour, then add 5 ml of conc. HCl and heat the solution to boiling. Add 25 ml 4% ammonium oxalate solution slowly with constant stirring to the hot solution, then neutralise the mixture by adding (1:1) aqueous ammonia dropwise with stirring till the solution is faintly alkaline, indicated by the change of colour from red to yellow and calcium oxalate starts precipitating. Heat just to boiling. Allow the solution to stand for about 30 minutes in warm condition on an asbestos board under low flame. Filter the precipitate carefully through a Whatman No. 42 filter paper. Wash the precipitate with cold ~0.1% ammonium oxalate solution to free it from chloride ion (test with AgNO_3 solution in nitric acid medium) and then with cold water to free it from oxalate ion (test with CaCl_2 solution in ammoniacal medium).

Dissolve the precipitate in hot 50 ml 4(N) H_2SO_4 and wash the filter paper with 50 ml hot distilled water. Heat the solution to $70^\circ - 80^\circ\text{C}$ and titrate with the standard ($\sim\text{N}/20$) KMnO_4 solution to a faint pink colour, that is stable for ~ 30 seconds.

Calculation :

$$\text{Strength of standard oxalic acid} = \left(\frac{w}{0.7879} \right) (\text{N}/20)$$

where, w = wt. of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ per 250 ml solution.

If 25 ml of standard oxalic acid $\equiv V_1$ ml of KMnO_4

$$\text{then, strength of } \text{KMnO}_4 = \left(\frac{25.w}{0.7879.V_1} \right) (\text{N}/20)$$

If 25 ml of sample Ca solution

$$\equiv V_2 \text{ ml of } \left(\frac{25.w}{0.7879.V_1} \right) (\text{N}/20) \text{ KMnO}_4$$

Then, 250 ml of sample Ca solution

$$\equiv 10.V_2 \text{ ml of } \left(\frac{25.w}{0.7879.V_1} \right) (\text{N}/20) \text{ KMnO}_4$$

$$\equiv \left(\frac{10 \times 25}{0.7879 \times 20} \right) \times \left(\frac{w.V_2}{V_1} \right) \text{ ml (N) KMnO}_4$$

$$\equiv 15.86 \times (w V_2/V_1) \text{ ml of (N) KMnO}_4$$

$$\equiv (0.02004 \times 15.86) \times (w.V_2/V_1) \text{ g. of Ca}$$

$$\equiv 0.3178. (w.V_2/V_1) \text{ g. of Ca}$$

$$\equiv (0.05004 \times 15.86) \times (w.V_2/V_1) \text{ g. of CaCO}_3$$

$$\equiv 0.7939 (w.V_2/V_1) \text{ g. of CaCO}_3$$

If the weight of the dolomite sample is w' g, then

$$\text{CaCO}_3 (\%) = 79.39 \times (w.V_2/w'V_1)$$

If sodium oxalate, $\text{Na}_2\text{C}_2\text{O}_4$ [strength : (w/0.8375) (N/20)] is used as the primary standard, similar calculation will give

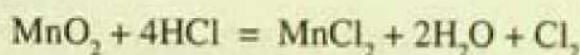
$$\text{CaCO}_3 (\%) = 73.81 \times (w V_2 / w' V_1)$$

where, w = wt. of $\text{Na}_2\text{C}_2\text{O}_4$ per 250 ml solution.

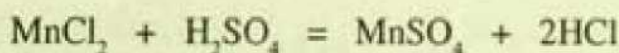
Experiment No. 6 : Estimation of manganese in Pyrolusite

Principle :

The manganese ore, pyrolusite, contains mainly MnO_2 and small amount of MnO . A known weight of finely ground pyrolusite is brought into solution by heating with hydrochloric acid. MnO_2 passes into solution by oxidising HCl to liberate Cl_2 .



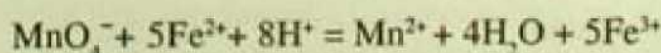
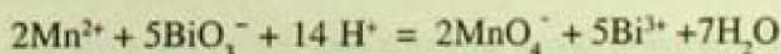
The solution is then boiled with conc. H_2SO_4 to remove the chloride as HCl ,



The resulting Mn^{II} -sulfate is then oxidised to MnO_4^- by bismuthate oxidation method or to MnO_2 by bromate oxidation method. Finally, MnO_4^- or MnO_2 as the case may be, is treated with a measured excess of standard Mohr's salt solution and the excess Mohr is back titrated with standard KMnO_4 solution in presence of H_3PO_4 .

Bismuthate oxidation method

Mn^{2+} is oxidised to MnO_4^- with an excess of sodium bismuthate (NaBiO_3) in 2-3 (N) H_2SO_4 acid medium. The excess bismuthate is then removed by filtration through a sintered-glass crucible or through an asbestos-pulp bed. The resulting MnO_4^- so obtained is estimated by adding a measured excess of standard Mohr's salt solution and back titrating the excess Mohr with a standard solution of KMnO_4 .

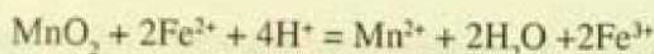
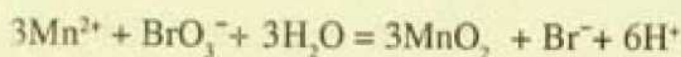


$$\therefore \frac{\text{MnO}_4^-}{5} \equiv \text{Fe}^{2+} \equiv \frac{\text{Mn}^{2+}}{5} \equiv \frac{\text{Mn}}{5} = \frac{54.94}{5} \text{ g. of Mn} = 10.988 \text{ g. of Mn}$$

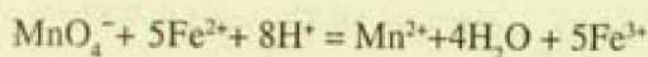
$$\therefore 1000 \text{ ml (N) KMnO}_4 \text{ solution} \equiv 10.988 \text{ g of Mn}$$

Bromate oxidation method

Mn^{II} is oxidised to MnO₂ by boiling with an excess of potassium bromate (KBrO₃) in dil. H₂SO₄ medium. Excess bromate is then removed by filtration and washing. Precipitated MnO₂ is then dissolved in a measured excess of standard Mohr's salt solution. The excess Mohr is then back titrating with a standard KMnO₄ solution.



$$\therefore \frac{\text{MnO}_2}{2} \equiv \frac{\text{Mn}^{2+}}{2} \equiv \text{Fe}^{2+}$$



$$\therefore \frac{\text{MnO}_4^-}{5} \equiv \frac{\text{Mn}}{5} \equiv \text{Fe}^{2+}$$

$$\therefore \frac{\text{MnO}_4^-}{5} \equiv \text{Fe}^{2+} \equiv \frac{\text{Mn}}{2} = \frac{54.94}{2} \text{ g. of Mn} = 27.47 \text{ g. of Mn}$$

$$\therefore 1000 \text{ ml (N) KMnO}_4 \text{ solution} \equiv 27.47 \times 1.01 \text{ g of Mn}$$

(1.01 is an empirical factor in this method of estimation)

Chemicals & apparatus required :

1. Oxalic acid or sodium oxalate (A.R.)
2. ~ (N/20) Mohr's salt solution
3. Syrupy phosphoric acid
4. Sodium bismuthate (A.R.), or, 5% (A.R.) KBrO₃ solution.
5. Filter paper : Whatman No, 41
6. G-3 sintered glass crucible or asbestos pulp bed.
7. Suction filtering system.

Procedure :

1. Prepare 250 ml of standard (N/20) oxalic acid or sodium oxalate solution by accurate weighing. (cf. Experiment No. 1).

2. Standardisation of KMnO_4 solution.

Pipette out an aliquot of 25 ml standard (N/20) oxalic acid or sodium oxalate solution in to a 250 ml conical flask, add 25 ml 4(N) H_2SO_4 . Heat the solution nearly to $70^\circ - 80^\circ\text{C}$ and then titrate with ($\sim\text{N}/20$) KMnO_4 solution in hot condition till a faint pink colour persists in the solution for ~ 30 seconds.

3. Standardisation of Mohr's salt solution :

Pipette out an aliquot of 25 ml Mohr's salt solution in a 250 ml conical flask, add 3 ml syrupy H_3PO_4 and 25 ml 4(N) H_2SO_4 and then titrate with a standard ($\sim\text{N}/20$) KMnO_4 solution till a faint pink colour persists in the solution for ~ 30 seconds.

4. Dissolution of pyrolusite :

Weigh out accurately $\sim 2.0\text{g}$ of finely ground dry pyrolusite ore into a 500 ml conical flask. Moisten the powder with minimum quantity of water, add 20 ml 1:1 HCl , heat (under fume hood) to dissolve the solid and then evaporate nearly to dryness over a low flame on an asbestos board. Repeat the process with 10 ml of 1:1 HCl , if necessary, and cool to room temperature. Finally fume the mixture with 10 ml conc. H_2SO_4 to drive off HCl completely. Cool and carefully dilute with 50 ml of water, boil to dissolve the sulphate salts and filter through a Whatmann No. 1 filter paper (if necessary) and collect the filtrate in a 250 ml volumetric flask. Wash the filter paper 4-5 times with 5 ml portions of cold 0.5(N) H_2SO_4 and make up the volume with distilled water. Acidity of the solution will be $\sim 1.4(\text{N})$.

5.(a) Estimation of Mn by bismuthate oxidation method :

Pipette out a 25 ml aliquot of the prepared solution in to a 250 ml beaker. Add 7-8 ml of conc. H_2SO_4 and dilute to 100 ml with water to adjust the acidity $\sim 3(\text{N})$. Oxidise by adding $\sim 0.5\text{ g}$ portions of sodium bismuthate, till some unreacted bismuthate is visible at the bottom of the beaker. Stir the mixture thoroughly. Filter the mixture through a bed of asbestos pulp or a sintered glass crucible (G-3) under gentle suction and collect the filtrate in a 500 ml clean Buchner flask. Wash with 10 ml portions of cold 2(N) H_2SO_4 solution till the washings are colourless. Add a measured excess (25/50/75 ml say. $25 \times x\text{ ml}$) of standard ($\sim\text{N}/20$) Mohr's salt solution using a pipette to discharge the permanganate colour. Add 5 ml of syrupy H_3PO_4 and back titrate the excess Mohr's salt solution with the standard (N/20) KMnO_4 solution till the first appearance of a permanent faint pink colour. Calculate the amount of Mn from the difference in titre values.

(b) Estimation of Mn by bromate oxidation method:

Pipette out 25 ml of the prepared solution in a 250 ml beaker. Add 2 ml conc. H_2SO_4 and dilute to 100 ml (to adjust the acidity to $\sim 1\text{N}$). Add 10 ml of 5% KBrO_3 solution. Heat the mixture to gentle boiling for 10-20 minutes, keeping the beaker covered with a watch glass and add water to replenish that lost by boiling. Allow the mixture to cool to room temperature and filter the precipitated MnO_2 carefully through a Whatman No. 41 filter paper. If any turbidity appears in the filtrate, refilter the first portion again through the same filter paper. Wash the beaker and the precipitate thoroughly with hot water, using 5 ml portion each time, till the washings are free from BrO_3^- (test with starch-KI in acidic medium). Transfer the precipitate of MnO_2 with the filter paper in the original beaker, add 25 ml 4(N) H_2SO_4 and measured excess (25/50/75 ml say, $25 \times x$ ml) of standard ($\sim \text{N}/20$) Mohr's salt solution using a pipette and stir to dissolve the brown precipitate of MnO_2 . Add 5 ml of syrupy H_3PO_4 and back titrate the excess Mohr's salt solution with standard ($\sim \text{N}/20$) KMnO_4 solution till the first appearance of faint pink colour. Calculate the amount of Mn from the difference in the titre values.

Calculation :

If 25 ml of (w/0.7879) ($\text{N}/20$) oxalic acid or (w/0.8375) ($\text{N}/20$) sodium oxalate

$\equiv V_1$ ml of S($\text{N}/20$) KMnO_4 solution, then,

$$S = \frac{w \times 25}{V_1 \times 0.7879} \quad (\text{if } \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \text{ is the primary standard})$$

$$\text{or, } S = \frac{w \times 25}{V_1 \times 0.8375} \quad (\text{if } \text{Na}_2\text{C}_2\text{O}_4 \text{ is the primary standard})$$

If 25 ml of ($\sim \text{N}/20$) Mohr's solution

$\equiv V_2$ ml of S ($\text{N}/20$) KMnO_4

and (25 x x) ml of ($\sim \text{N}/20$) Mohr's solution

$\equiv V_3$ ml of S ($\text{N}/20$) KMnO_4 + MnO_2 obtained from V ml of the sample solution,

then, MnO_2 obtained from V ml of sample solution

$$\equiv (x \cdot V_2 - V_3) \text{ ml of S } (\text{N}/20) \text{ } \text{KMnO}_4$$

$$\therefore \frac{\text{MnO}_4^-}{5} \equiv \text{Fe}^{2+} \equiv \frac{\text{MnO}_2}{2} \equiv \frac{\text{Mn}}{2} \equiv \frac{54.94}{2} \text{ g. of Mn} \equiv 27.47 \text{ g. of Mn.}$$

$$\therefore 1000 \text{ ml (N) KMnO}_4 \equiv 27.47 \text{ g. of Mn}$$

$$\text{Actually, } 1000 \text{ ml (N) KMnO}_4 \equiv 1.01 \times 27.47 \text{ g. of Mn}$$

$$(1.01 = \text{empirical factor})$$

$$\therefore (xV_2 - V_3) \text{ ml of S(N/20) KMnO}_4 \equiv \frac{1.01 \times 27.47 \times (xV_2 - V_3) \times S}{1000 \times 20} \text{ g. of Mn}$$

$$\therefore \text{Total Mn} = \frac{1.01 \times 27.47 \times (xV_2 - V_3) \times S \times 250}{1000 \times 20 \times V} \text{ g. of Mn}$$

where, S = factor of (N/20) KMnO₄ solution.

Experiment No. 7 : Estimation of Fe and Ca in mixture

Principle :

If iron is present as Fe^{III}, it has to be first of all reduced to Fe^{II} by SnCl₂ method or with Al - foil. Fe^{II} is then titrated with a standard solution of KMnO₄ in presence of Zimmerman-Reinhardt reagent (H₃PO₄ + H₂SO₄ + MnSO₄).



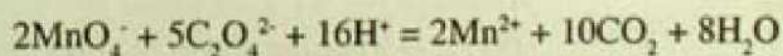
$$\therefore \frac{\text{MnO}_4^-}{5} \equiv \text{Fe}$$

$$\therefore 1000 \text{ ml (N) KMnO}_4 \text{ solution} \equiv 55.847 \text{ g. of Fe.}$$

For estimation of calcium, iron (Fe³⁺) is to be first separated as ferric hydroxide. From the filtrate, Ca²⁺ is precipitated as calcium oxalate, which after separation from excess oxalate and chloride, is dissolved in hot dil. H₂SO₄, when an equivalent amount of oxalic acid is liberated, which is then titrated with standard KMnO₄ solution.



$$\therefore \text{C}_2\text{O}_4^{2-} \equiv \text{Ca}$$



$$\therefore \frac{\text{MnO}_4^-}{5} \equiv \frac{\text{C}_2\text{O}_4^{2-}}{2} \equiv \frac{\text{Ca}}{2}$$

$\therefore (1/5) \text{MnO}_4^- \equiv (1/2) \text{Ca}^{2+} \equiv 1 \text{ equivalent} \equiv (40.08/2) \text{ g. of Ca}$

$\therefore 1000 \text{ ml (N) KMnO}_4 \text{ solution} \equiv 20.04 \text{ g. of Ca.}$

Chemicals required :

- | | |
|--|---------------------------------------|
| 1) Oxalic acid/sodium oxalate (A.R.) | 6) 4% Amminium oxalate solution |
| 2) 15% SnCl_2 solution / Al-fair (A.R.) | 7) 4(N) H_2SO_4 |
| 3) 5% HgCl_2 solution | 8) Phthalate buffer solution (pH = 4) |
| 4) Z-R-reagent | 9) Whatman No. 41 & 42 filter papers. |
| 5) Methyl red indicator | |

Procedure :

1. Transfer the sample solution quantitatively in to a 250 ml volumetric flask, and make up to the mark with distilled water, and mix uniformly.
2. Prepare 250 ml of standard (N/20) oxalic acid (or, sodium oxalate) solution by accurate weighing. Standardise the (\sim N/20) KMnO_4 solution against standard (N/20) oxalic acid (or, sodium oxalate) solution as usual. (cf. Experiment No. 1).

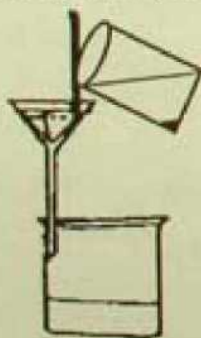
3. Estimation of Iron :

Pipette out 25 ml of the stock solution in a 500 ml conical flask. Neutralise with 1:1 aqueous NH_3 to obtain a faint turbidity. To this neutral solution add an equal volume of conc. HCl to adjust 6(N) HCl acidity. Heat just to boiling and reduce Fe^{3+} ion with SnCl_2 solution adding dropwise until the yellow colour is just discharged and finally add a drop in excess. Cool under tap water to room temperature. Add 10 ml of 5% HgCl_2 solution **at a time**, shake and allow to stand for 2-3 minutes, when a silky white precipitate of Hg_2Cl_2 is formed. Dilute to 300 ml with water. Add 25 ml of Z-R reagent. Titrate with standard (N/20) KMnO_4 solution until the solution just turns pale pink colour, which persists for ~ 15 seconds. (Fe^{III} may also be reduced to Fe^{II} by Al-foil. See Experiment No. 3)

4. Estimation of Calcium :

(a) Separation of Fe^{III} :

Pipette out 25 ml. of the stock solution in to a 250 ml conical flask. Dilute it to 100 ml., add 1.0 g. NH_4Cl and heat the solution nearly to boiling. Add (1 : 1) aqueous ammonia to make the solution just ammoniacal, when ferric hydroxide is precipitated. Allow the brown precipitate to settle and filter through Whatman No. 41 filter paper and collect the filtrate in a 500 ml in a beaker. Wash the precipitate twice with 1% NH_4Cl solution containing a few drops of ammonia. Preserve the combined filtrate and washings for estimation of calcium.



filtration

Dissolve the brown precipitate of ferric hydroxide in minimum quantity of hot (1 : 1) HCl, wash the filter paper with hot water and collect the solution and the washings in the original conical flask. Dilute the solution to 100 ml, reprecipitate with 1:1 aqueous ammonia, refilter through the same filter paper and collect the filtrate in the same beaker containing the first filtrate and the washings. Wash the precipitate 2-3 times with 1% NH_4Cl solution containing little ammonia as before. Use the combined filtrate and the washings for estimation of calcium.

Note : The precipitated ferric hydroxide may be dissolved in hot 6(N)HCl (30 ~ 50 ml) and after reduction of Fe^{3+} to Fe^{2+} by SnCl_2 or Al-foil or Jones reductor method, the resulting Fe^{2+} may be estimated by titrating with a standard (~ N/20) solution of KMnO_4 in presence of Z-R reagent.

Reduce the volume of the combined filtrate and the washings to about 200 ml by boiling. Add a few drops of methyl red indicator, and neutralise with (1:1) HCl till the solution is just acidic (red), then add 5 ml conc. HCl and heat the solution to boiling. Add with constant stirring 25 ml of 4% ammonium oxalate solution slowly to the hot solution and then render the solution ammoniacal by adding (1:1) aqueous ammonia dropwise with stirring, till the colour of the solution changes from red to yellow. Heat to boiling and allow the solution to stand for about 30 minutes in warm condition on an asbestos board under low flame. Filter the precipitated calcium oxalate through a Whatman No. 42 filter paper, wash with cold 0.1% ammonium oxalate solution to free it from chloride ion (test with AgNO_3 solution in nitric acid medium) and then with cold water to free it from oxalate ion (test with CaCl_2 solution in ammoniacal medium).

Dissolve the precipitate in hot 50 ml of 4(N) H_2SO_4 and wash the filter paper and the beaker with 50 ml of distilled water. Heat the solution to $70^\circ - 80^\circ\text{C}$ and titrate the solution with standard (~N/20) KMnO_4 solution to a faint pink colour that persists for 30 seconds.

Alternative method of estimation of Ca^{2+} in presence of Fe^{3+} without separation of ferric hydroxide

Estimation of Calcium :

Pipette out 25 ml of the stock solution in to a 500 ml beaker, add 5 ml of conc. HCl and dilute to 50 ml. Heat the solution nearly to boiling and add 100 ml of saturated ammonium oxalate solution, also almost boiling, and 5 drops of methyl red indicator. Add dropwise 1:1 aqueous NH_3 very slowly with constant stirring till the colour of the indicator is the same as that of an equal volume of standard phthalate buffer solution (pH 4) containing the same amount (5 drops) of the indicator. Allow the mixture to stand for 20-30 minutes in hot

condition, when calcium oxalate precipitates, while Fe^{III} remains in solution as its oxalato complex. Filter through Whatman No. 42 filter paper, wash with ~100 ml ice-cold water taking small portions (~10 ml) at a time, till the washings are free from oxalate ion (test with CaCl_2 solution in ammoniacal medium) and Cl^- (test with AgNO_3 / HNO_3). Transfer the precipitate quantitatively into the original beaker as usual and dissolve the same in hot 50 ml of 4(N) H_2SO_4 , wash the filter paper and the beaker with 50 ml of hot distilled water. Heat the solution to $70^\circ - 80^\circ\text{C}$ and titrate the liberated oxalic acid with standard (~N/20) KMnO_4 solution to a light pink end point that persists for ~ 30 seconds.

Experiment No. 8 : Analysis of Portland Cement

(a) Estimation of Fe_2O_3 in cement

Principle :

Portland cement contains CaO , MgO , SiO_2 , Al_2O_3 , Fe_2O_3 etc. along with traces of Na_2O and K_2O . A weighed quantity of finely powdered cement is brought into solution by heating with 1:1 HCl . Then Fe^{3+} , present in the solution, is reduced to Fe^{2+} by SnCl_2 or Al -foil / or Jones reductor method. Fe^{2+} thus obtained is then titrated with standard KMnO_4 solution in presence of Z-R reagent ($\text{MnSO}_4 + \text{H}_2\text{SO}_4 + \text{H}_3\text{PO}_4$).



$$\therefore \frac{\text{MnO}_4^-}{5} \equiv \text{Fe}^{2+} \equiv \text{Fe}^{3+} \equiv \frac{\text{Fe}_2\text{O}_3}{2} = \frac{159.692}{2} \text{ g. of } \text{Fe}_2\text{O}_3$$

$$\therefore 1000 \text{ ml (N) } \text{KMnO}_4 \text{ solution} \equiv 79.846 \text{ g. of } \text{Fe}_2\text{O}_3$$

Chemicals required : Same as Experiment No. 3.

Procedure :

1. Prepare 250 ml standard (N/50) oxalic acid (or, sodium oxalate) by accurate weighing.
2. Standardise the (~N/50) KMnO_4 solution against the standard (N/50) oxalic acid or, sodium oxalate solution. (see Experiment No. 1)
3. **Dissolution of Cement :**

Weigh out accurately about 1 g. of finely powdered cement in a 250 ml beaker. Add 100 ml water and 25 ml of conc. HCl , partially cover with a clock glass. Heat the mixture gently and break up lumps if any, with a glass rod. When the sample of cement has reacted completely, allow the mixture to cool to room temperature and transfer the same

quantitatively into a 250 ml volumetric flask by washing with water. Make up the volume to the mark with distilled water, mix the solution uniformly and allow to settle for 10 minutes.

4. Estimation of Fe :

Pipette out 50 ml of the supernatant liquid of the stock solution in to a 500 ml conical flask and add 25 ml of conc. HCl. Reduce Fe^{3+} to Fe^{2+} by any of the following methods.

(i) SnCl_2 method : Heat just to boiling, reduce Fe^{3+} ion with SnCl_2 solution adding dropwise until the yellow colour is just discharged and finally add a drop in excess. Cool under tap water to room temperature. Add 10 ml of 5% HgCl_2 solution at a time with vigorous shaking. Allow to stand for 2-3 minutes.

or, (ii) Reduction by Al-foil : Add a few pieces of Al-foil to the Fe^{3+} solution. Heat carefully and swirl the mixture till the yellow colour is discharged and the unreacted Al-foils dissolve completely to give a clear solution.

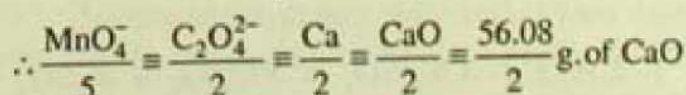
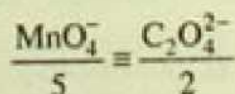
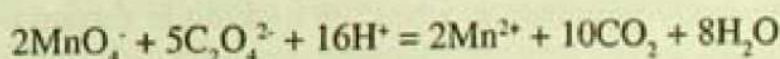
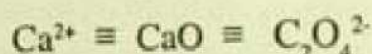
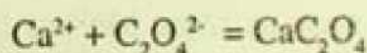
Dilute the above solution obtained from (i)/(ii) to 300 ml with water. Add 25 ml of Zimmermann-Reinhardt solution. Titrate with standard ($\sim \text{N}/50$) KMnO_4 solution till the appearance of light pink colour.

Calculate the amount and % of Fe_2O_3 in the sample. (cf. Experiment No. – 3).

8(b) Estimation of CaO in Portland cement

Principle :

To estimate CaO in the digested HCl solution of Portland cement [Experiment No. 8(a)], Fe^{3+} is first separated from the solution by precipitating it as hydroxide. From the filtrate Ca^{2+} is precipitated as calcium oxalate, which after filtration and washing free from excess oxalate and chloride, is dissolved in hot dil. 4(N) H_2SO_4 , when an equivalent amount of oxalic acid is liberated which is then titrated with standard KMnO_4 solution.



\therefore 1000 ml (N) KMnO_4 solution \equiv 28.04 g of CaO

Chemicals required : Same as Experiment No. 7.

Procedure :

(a) Separation of Fe^{III} :

Pipette out 50 ml of the stock solution in a 250 ml conical flask, dilute it to 100 ml, add 1.0 g. NH_4Cl and heat the solution nearly to boiling. Add (1 : 1) aqueous ammonia to make the solution ammoniacal. Allow the precipitate to settle and filter through Whatman No. 41 filter paper. Collect the filtrate in a 500 ml beaker. Wash the precipitate twice with 1% NH_4Cl solution containing a few drops of ammonia. Preserve the filtrate and the washings for estimation of calcium. Dissolve the precipitate of ferric hydroxide in minimum volume of hot (1:1) HCl , reprecipitate with 1:1 aqueous NH_3 , refilter through the same filter paper and wash as before. Collect the filtrate and the washings in the same beaker containing the calcium solution. Preserve the combined filtrate and the washings for estimation of calcium.

(b) Precipitation of Ca^{2+} as calcium oxalate : (Follow the procedure described in case of Fe-Ca mixture, Experiment No. 7).

(c) Conversion of calcium oxalate into equivalent amount of oxalic acid and its estimation : Dissolve the precipitate of calcium oxalate in hot 50 ml of 4(N) H_2SO_4 . Wash and dilute to 100 ml with hot water. Heat the solution to $70^\circ - 80^\circ\text{C}$ and titrate the solution with standard ($\sim\text{N}/50$) KMnO_4 solution to a faint pink colour, that is stable for ~ 30 seconds.

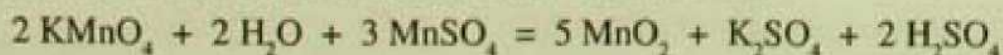
Notes :

1. During titration of oxalic acid with KMnO_4 , the temperature should be maintained within $70^\circ - 80^\circ\text{C}$. The solution should not be boiled, as oxalic acid may decompose at high temperature.

2. (a) The reaction between oxalic acid and KMnO_4 is very slow at the start. Titration is carried out at $70^\circ - 80^\circ\text{C}$ at which the reaction is sufficiently rapid to enable titration. The reaction becomes quite fast as soon as some Mn^{2+} is formed, which acts as a catalyst (*autocatalysis*).

(b) Hot condition is also required to decompose the deep purple Mn^{III} complex, $[\text{Mn}^{\text{III}}(\text{C}_2\text{O}_4)_3]^{3-}$, which may be formed owing to local excess of KMnO_4 during titration. The complex is thermally unstable, so when the titration is carried out above 60°C , the complex decomposes.

3. At the equivalence point, the pink colour due to slight excess of KMnO_4 persists for ~ 30 seconds. The pink colour may be unstable due to the reaction :

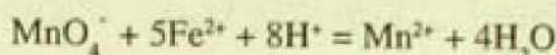


Experiment No. 9 : Analysis of basic slag

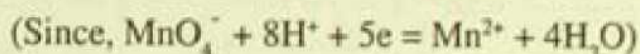
(a) Estimation of Fe_2O_3 in basic slag

Principle :

Basic slag contains Fe_2O_3 , CaO , MgO , MnO , Al_2O_3 , P_2O_5 , V_2O_5 , SiO_2 etc. A known weight of finely powdered basic slag is brought into solution by digesting with hot 1:1 HCl . Fe^{3+} is then reduced to Fe^{2+} and finally titrated with standard KMnO_4 solution in presence of Z-R reagent ($\text{H}_3\text{PO}_4 + \text{H}_2\text{SO}_4 + \text{MnSO}_4$).



$$\therefore \frac{\text{MnO}_4^-}{5} \equiv \text{Fe}^{2+} \equiv \frac{\text{Fe}_2\text{O}_3}{2} \equiv \frac{159.692}{2} \text{ g. of } \text{Fe}_2\text{O}_3$$



$$\therefore 1000 \text{ ml (N) } \text{KMnO}_4 \text{ solution} \equiv 79.846 \text{ g of } \text{Fe}_2\text{O}_3$$

Chemicals required : Same as Experiment No. 3 and Whatman No. 40 filter paper.

Procedure :

1. *Dissolution of basic slag :* Attack ~1.0 g of finely powdered basic slag with 30 ml of 6(N) HCl in a 250 ml beaker, heat gently on an asbestos board till dissolution. To remove SiO_2 , evaporate the solution to dryness over a low flame (under a fume hood) and repeat the process twice with two other 10 ml portions of the same acid. Finally fume the mixture with 10 ml of conc. H_2SO_4 to free it from Cl^- , cool, dilute carefully with 100 ml water and heat to dissolve the resulting sulphates. Cool to room temperature and filter through Whatman No. 40 filter paper into a 250 ml volumetric flask, wash with very dilute (~0.1 N) H_2SO_4 and make up the volume to 250 ml with distilled water. Acidity of the solution will be ~1.4 – 1.5 (N).

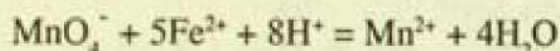
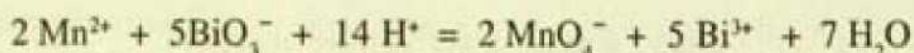
2. *Estimation of Fe :* Pipette out 50 ml of the prepared solution in a 500 ml conical flask, reduce its volume to ~25 ml by evaporation, add 12-15 ml of conc. HCl to adjust 6(N) acidity. Heat just to boiling and reduce Fe^{3+} ion with SnCl_2 solution or using Al-foil as usual (cf. Experiment No. 3). Cool under tap water to room temperature, and dilute to ~300 ml with water. Add 25 ml Zimmermann-Reinhardt reagent and titrate with the standard (~N/20) KMnO_4 solution till a light pink end point that persists for ~15 seconds.

Standardise the (~N/20) KMnO_4 solution against standard (N/20) oxalic acid sodium oxalate (cf. Experiment No. 1) and calculate the % of Fe_2O_3 in the sample.

9(b) Estimation of MnO in basic slag

Principle :

Mn²⁺ can be estimated in presence of Fe³⁺ and other constituents after oxidising Mn²⁺ to MnO₄⁻ with sodium bismuthate. After removing the excess bismuthate by filtration through sintered-glass crucible (G-3) or through asbestos-pulp bed, the resulting MnO₄⁻ is treated with a measured excess of standard Mohr's salt solution, and the excess Mohr is then back titrated with standard KMnO₄ solution in presence of Zimmermann-Reinhardt reagent.



$$\therefore \frac{\text{MnO}_4^-}{5} \equiv \text{Fe}^{2+} \equiv \frac{\text{MnO}}{5} \equiv \frac{70.9394}{5} \text{ g. of MnO}$$

$$\therefore 1000 \text{ ml (N) Mohr's salt solution} \equiv 14.1879 \text{ g of MnO}$$

Chemicals required : Same as Experiment No. 6.

Procedure :

- (i) Dissolution of basic slag : Same as Experiment No. 9(a).
- (ii) Estimation of Mn after oxidation with bismuthate :

Pipette out 50 ml of the stock solution in a 250 ml beaker, add 5-6 ml of conc. H₂SO₄ to adjust the acidity to ~ 3(N) and cool to room temperature. Oxidise with about ~0.5 g of sodium bismuthate. Note that some brown bismuthate particles are visible at the bottom of the solution. Filter through a sintered-glass crucible (G-3) or through an asbestos pulp bed into a 500 ml clean Buchner flask under low suction. Wash with 5 ml portions of 0.5(N) H₂SO₄ till the washings are colourless.

To the combined filtrate and the washings, add a measured excess (25/50/75 ml say (25 × x) ml) of standard (~N/20) Mohr's salt solution to discharge the permanganate colour. Add 5 ml of syrupy H₃PO₄ and titrate with the standard (~N/20) KMnO₄ solution to a light pink end point that persists for ~30 seconds.

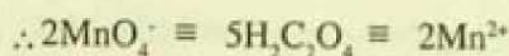
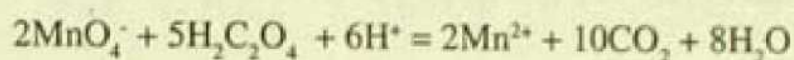
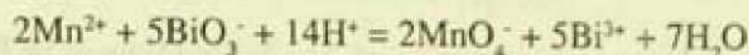
- (iii) Standardise the (~N/20) KMnO₄ solution against standard (N/20) oxalic acid/sodium oxalate (cf. Experiment No. 1) and the (~N/20) Mohr's salt solution against the standard (N/20) KMnO₄ solution (cf. Experiment No. 2).

- (iv) Calculate the % MnO in the sample (see Experiment No. 6).

Experiment No. 10 : Estimation of manganese in cast iron

Principle:

Cast iron may contain 0.2 – 1.0% of Mn. A weighed quantity of cast iron is brought into solution by digesting with boiling 4(N) sulfuric acid. The resulting solution will contain Fe^{2+} and Mn^{2+} . On oxidation by sodium bismuthate Mn^{2+} is oxidised to MnO_4^- and Fe^{2+} is oxidised to Fe^{3+} and other reducing substances present are also oxidised. MnO_4^- so formed can be estimated by treating it with a measured excess of standard oxalic acid solution and back titrating the excess oxalic acid with a standard KMnO_4 solution.



$$\therefore \frac{\text{MnO}_4^-}{5} \equiv \frac{\text{H}_2\text{C}_2\text{O}_4}{2} \equiv \frac{\text{Mn}^{2+}}{5} \equiv \frac{\text{Mn}}{5} \equiv \frac{54.94}{5} \text{ g. of Mn} \equiv 10.988 \text{ g. of Mn}$$

$$\therefore 1000 \text{ ml (N) } \text{KMnO}_4 \text{ solution} \equiv 10.988 \text{ g. of Mn}$$

Chemicals required : Same as Experiment No. 6.

Procedure :

1. Prepare 250 ml standard (N/20) oxalic acid solution by accurate weighing. (cf. Experiment No. 1).
2. *Standardisation of the KMnO_4 solution :* (cf. Experiment No. 1).
3. *Dissolution of cast iron :*

Attack ~1.0 g. of cast iron with 50 ml of 4(N) H_2SO_4 acid in a 250 ml beaker and heat gently on an asbestos board till dissolution of the metal (till the reaction with acid subsides). Some carbon particles may remain undissolved. Dilute to ~ 100 ml, cool to room temperature, filter through a Whatman No. 1 filter paper, wash with 2(N) H_2SO_4 . Collect the filtrate and the washings in a 250 volumetric flask and make the volume up to the mark with 2(N) H_2SO_4 .

4. *Estimation of Mn :*

Pipette out an aliquot of 25 ml from the stock solution in a 250 ml beaker, add 3-4 ml conc. H_2SO_4 and dilute to 100 ml to adjust 3(N) acidity. Add a pinch of bismuthate to initiate oxidation, when the solution assumes a pink colour, stir the mixture for 2-3 minutes to oxidise any reducing matter. Discharge the pink colour or any turbidity (due to MnO_2) by adding drops of dilute Mohr's salt solution in 2(N) H_2SO_4 . Cool to 15°-20°C and add ~ 0.5 g

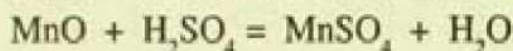
of sodium bismuthate to the clear solution and stir for 5-10 minutes. Filter through an asbestos pulp bed filter or through a G-3 sintered glass crucible using gentle suction, wash with 10 ml portions of 2(N) H_2SO_4 , till the washings are colourless. Treat the resulting MnO_4^- solution with measured excess (25/50/75 ml as required) of standard (N/20) oxalic acid, heat to $70^\circ\text{--}80^\circ\text{C}$ to discharge the pink colour due to permanganate. Back titrate the excess oxalic acid with standard ($\sim\text{N}/20$) KMnO_4 solution to a light pink end point that is stable for ~ 30 seconds.

Calculate the % of Mn in the sample of steel (cf. Experiment No. 6).

Experiment No. 11 : Estimation of Available Oxygen in Pyrolusite

Principle :

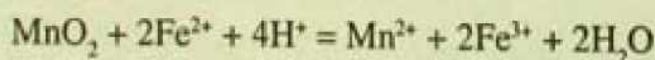
The manganese ore pyrolusite mainly contains MnO_2 along with some MnO , Fe_2O_3 etc. Available oxygen in pyrolusite refers to the oxygen or oxidising equivalent liberated by the action of dilute acids and is expressed in terms of percentage by weight of the pyrolusite.



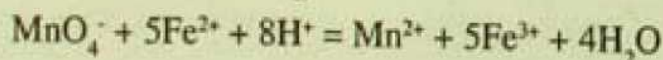
$$\therefore \text{MnO}_2 \equiv \frac{1}{2} \text{O}_2 \equiv \text{O} \equiv 15.9984 \text{ g. of oxygen}$$

In acid medium MnO_2 quantitatively oxidises reducing agents like oxalic acid, Mohr's salt etc. To determine the available oxygen in pyrolusite, a known weight of the ore is treated with a measured excess of standard Mohr's salt or oxalic acid solution in dilute 2(N) H_2SO_4 medium to dissolve the ore completely. The excess Mohr's salt or the oxalic acid is then back titrated with a standard KMnO_4 solution. The amount of available oxygen is obtained from the difference in titre values.

(a) Mohr's salt method :



$$\therefore \frac{\text{MnO}_2}{2} \equiv \text{Fe}^{2+}$$

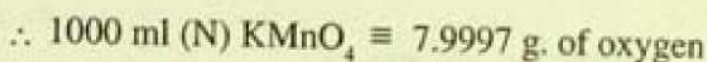
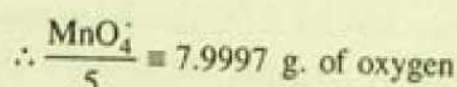
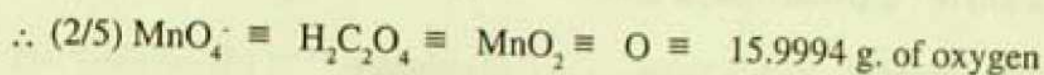
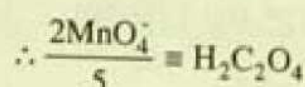
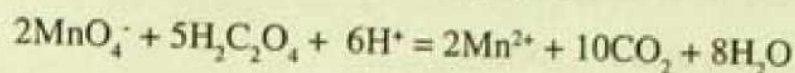
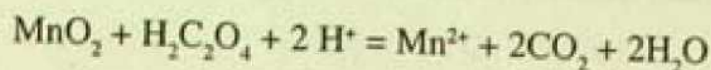


$$\therefore \frac{\text{MnO}_4^-}{5} \equiv \text{Fe}^{2+}$$

$$\therefore \frac{\text{MnO}_4^-}{5} \equiv \text{Fe}^{2+} \equiv \frac{\text{MnO}_2}{2} \equiv \frac{1}{2} \left(\frac{1}{2} \text{O}_2 \right) \equiv \frac{\text{O}}{2} \equiv \frac{15.9994}{2} \text{ g. of oxygen}$$

$$\therefore 1000 \text{ ml (N) } \text{KMnO}_4 \equiv 7.9997 \text{ g. of oxygen.}$$

(b) Oxalic acid method :



Chemicals required :

- (N/20) Standard oxalic acid solution : To be prepared by accurate weighing.
- (~ N/20) KMnO_4 solution.
- 4 (N) H_2SO_4
- (~ N/20) Mohr's salt solution
- Syrupy H_3PO_4 (85%).

Procedure :

1. *Standardisation of KMnO_4 solution :*

Pipette out 25ml of the standard (N/20) oxalic acid solution in a 250 ml conical flask, add 25 ml 4(N) H_2SO_4 , heat nearly to $70^\circ - 80^\circ\text{C}$ and then titrate with the KMnO_4 solution in the hot condition up to a faint pink colour that persists for ~30 seconds. (Titre = V_1 ml)

2. *Estimation of available O_2 in Pyrolusite:*

Transfer the given quantity (less than ~ 0.1 g) of pyrolusite ore into a 250 ml conical flask, add 50ml of 4(N) H_2SO_4 followed by 50 ml (say $25 \times x$ ml) of standard (N/20) oxalic acid solution using a pipette. Cover the flask with a short stem-funnel, heat the flask gently on an asbestos board till all the black particles of pyrolusite dissolve. Back titrate the excess oxalic acid in the hot condition ($70^\circ - 80^\circ\text{C}$) with standard (~ N/20) KMnO_4 solution up to the first appearance of faint pink colour that persists for ~ 30 seconds.

3. Calculate the total quantity of available oxygen in the supplied pyrolusite sample.

Calculation :

If, w. g. of pyrolusite is taken for analysis,

strength of oxalic acid = f. (N/20).

25 ml of f. (N/20) oxalic acid $\equiv V_1$ ml of KMnO_4

\therefore Strength of KMnO_4 solution = $(25.f/V_1)$ (N/20)

If $(25 \times x \text{ ml})$ of f. (N/20) oxalic acid

$\equiv V_2$ ml of $\frac{25.f}{V_1}$ (N/20) KMnO_4 + w.g. of pyrolusite

Then, w.g. of pyrolusite solution

$\equiv (V_1 \times x - V_2)$ ml of $\frac{25.f}{V_1}$ (N/20) KMnO_4

$\equiv \frac{(V_1 \times x - V_2) \times 25.f}{V_1 \times 20}$ ml of (N) KMnO_4

$\equiv \frac{7.9997 \times (V_1 \times x - V_2) \times 25.f}{1000 \times V_1 \times 20}$ g. of oxygen

(\because 1000 ml (N) $\text{KMnO}_4 \equiv 7.9997$ g. of oxygen)

Available oxygen (%)

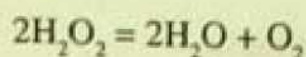
$\equiv \frac{7.9997 \times (V_1 \times x - V_2) \times 25.f}{1000 \times V_1 \times 20 \times w} \times 100(\%)$

A similar calculation may be performed for the Mohr's salt method. Mohr's salt solution (\sim N/20) has to be standardised against standard (N/20) KMnO_4 solution (cf. Experiment No. 2).

Experiment No. 12 : Estimation of the strength of H_2O_2

Principle :

The concentration of a sample of H_2O_2 is generally expressed as *volume* strength. Thus by 20 *volume* H_2O_2 we mean that O_2 produced due to decomposition of 1 ml of the sample of H_2O_2 occupies 20 c.c at NTP.



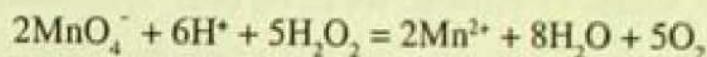
$$\therefore 68 \text{ g. of } \text{H}_2\text{O}_2 \equiv 22400 \text{ c.c of } \text{O}_2 \text{ at NTP}$$

$$\therefore 1 \text{ g. of } \text{H}_2\text{O}_2 \equiv \frac{22400}{68} \text{ c.c of } \text{O}_2 \text{ at NTP}$$

$$\therefore 100 \text{ ml of } 1\% \text{ } \text{H}_2\text{O}_2 \equiv \left(\frac{22400}{68} \right) \text{ volume of } \text{O}_2 \text{ at NTP.}$$

$$\therefore 1 \text{ ml } 1\% \text{ } \text{H}_2\text{O}_2 \equiv \left(\frac{224}{68} \right) \text{ volume } \text{H}_2\text{O}_2$$

The Strength of a H_2O_2 sample may be determined either by permanganometric or by iodometric titration. In permanganometry, a known volume of H_2O_2 is titrated with a standard solution of KMnO_4 in dilute H_2SO_4 medium, when KMnO_4 quantitatively oxidises H_2O_2 to O_2 according to,



$$\therefore (1/5) \text{MnO}_4^- \equiv (1/2) \text{H}_2\text{O}_2 \equiv (34/2) \text{ g. of } \text{H}_2\text{O}_2 \equiv 1 \text{ equivalent}$$

$$\therefore 1000 \text{ ml of (N) } \text{MnO}_4^- \text{ solution} \equiv 17.0 \text{ g. of } \text{H}_2\text{O}_2$$

Chemicals required :

- Standard (N/20) sodium oxalate or oxalic acid solution, to be prepared by accurate weighing.
- 4(N) H_2SO_4
- Sample H_2O_2 solution : Take 10 ml of the '20 volume' H_2O_2 sample by means of a burette into a 250 ml volumetric flask, dilute with distilled water upto the mark and mix uniformly.

Procedure :

- Standardisation of KMnO_4 solution: (cf. Experiment No. 1).
- Estimation of H_2O_2 :

Pipette out 25 ml. of the sample H_2O_2 solution in a 250 ml conical flask, add 25 ml of 4(N) H_2SO_4 and titrate with the standard (N/20) KMnO_4 solution to the first permanent faint pink colour that persists for ~ 30 seconds.

3. Calculate the volume strength of the H_2O_2 sample.

Calculation :

If w g. of oxalic acid is present in 250 ml solution, then strength of oxalic acid = $(w/0.7879) (N/20)$.

If 25 ml of $(w/0.7879) (N/20)$ oxalic acid

$$\equiv V_1 \text{ ml of } \text{KMnO}_4 \text{ solution of strength}(S)$$

then, strength of KMnO_4 solution,

$$S = \frac{25 \times w}{V_1 \times 0.7879} (N/20)$$

Now, 1000 ml of $(N) \text{KMnO}_4 \equiv 17 \text{ g. of } \text{H}_2\text{O}_2$

If V_2 ml of $(S) \text{KMnO}_4$ solution is required for 25 ml of H_2O_2 solution, then,

$$V_2 \text{ ml of } (S) \text{KMnO}_4 \equiv \left(\frac{17 \times V_2 \times S}{1000} \right) \text{ g. of } \text{H}_2\text{O}_2$$

\therefore 25 ml of H_2O_2 solution contains $(0.017 \times V_2 \times S) \text{ g. of } \text{H}_2\text{O}_2$

\therefore 100 ml of H_2O_2 solution contains $(0.017 \times V_2 \times S \times 4) = (0.068 \times V_2 \times S) \text{ g. of } \text{H}_2\text{O}_2$

\therefore % strength of H_2O_2 solution = $(0.068 \times V_2 \times S) \%$

$$\therefore 1\% \text{H}_2\text{O}_2 \equiv \left(\frac{224}{68} \right) \text{ volume } \text{H}_2\text{O}_2$$

$$\begin{aligned} \therefore (0.068 \times V_2 \times S) \% \text{H}_2\text{O}_2 &= \left(\frac{224}{68} \times 0.068 \times V_2 \times S \right) \text{ volume } \text{H}_2\text{O}_2 \\ &= (0.224 \times V_2 \times S) \text{ volume } \text{H}_2\text{O}_2 \\ &= \left(\frac{0.224 \times V_2 \times 25 \times w}{V_1 \times 0.7879 \times 20} \right) \text{ volume } \text{H}_2\text{O}_2 \end{aligned}$$

Note : It is advised to use a fairly high acidity and a reasonably slow rate of addition of KMnO_4 solution to prevent the formation of MnO_2 which is an active catalyst for the decomposition of H_2O_2 .

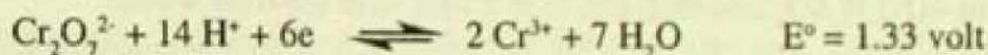
Chapter - 5

Redox Titrimetric Estimations Using Standard Potassium Dichromate Solution

Experiment No. 1: Preparation of (N/20) $K_2Cr_2O_7$ solution and standardisation of Mohr's salt, $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$, solution

Principle :

A standard solution of potassium dichromate ($K_2Cr_2O_7$) may be prepared by accurate weighing, since it is a primary standard substance. In acid medium, $K_2Cr_2O_7$ acts as an oxidant,



$$\therefore \text{Equivalent weight of } K_2Cr_2O_7 = K_2Cr_2O_7 / 6 = 294.18 / 6 = 49.03$$

$$\therefore 1000 \text{ ml (N) } K_2Cr_2O_7 \text{ solution} \equiv 49.03 \text{ g. of } K_2Cr_2O_7$$

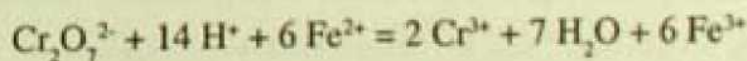
In acid medium $K_2Cr_2O_7$ quantitatively oxidises Fe^{2+} present in Mohr's salt to Fe^{3+}



$$\begin{aligned} \therefore \text{Equivalent weight of Mohr's salt} &= \frac{F.W.}{1} \\ &= \frac{(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O}{1} = \frac{392.143}{1} = 392.143 \end{aligned}$$

Mohr's salt solution may be standardised by titrating with a standard $K_2Cr_2O_7$ solution in H_2SO_4 acid medium in presence of NH_4HF_2 (or H_3PO_4), using barium diphenylaminesulphonate (BDS) as indicator upto a violet end point.

The overall reaction is,



$$\therefore [Cr_2O_7^{2-}] \equiv 6 [Fe^{2+}]$$

$$\text{or, } [Cr_2O_7^{2-}]/6 \equiv [Fe^{2+}]$$

\therefore 1000 ml of (N) $K_2Cr_2O_7$ solution $\equiv [Fe^{2+}] \equiv (NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$

$$\equiv 55.847 \text{ g. } Fe^{2+} \equiv 392.143 \text{ g. } (NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$$

If V_1 ml of S_1 (N) $K_2Cr_2O_7$ completely oxidises V_2 ml of S_2 (N) Mohr's salt solution then,

$$V_1 \times S_1 = V_2 \times S_2$$

\therefore Strength of Mohr's salt solution (S_2) = $[V_1 S_1 / V_2]$ (N)

$$\text{Strength in g. Lit}^{-1} = S_2 \times 392.143.$$

Chemicals required :

- A. R. $K_2Cr_2O_7$
- $\sim(N/20)$ Mohr's Salt solution : Dissolve about 19.6 g of A. R. Mohr's salt in 500 ml of 4(N) H_2SO_4 and then dilute to 1 litre with distilled water.
- 4(N) H_2SO_4 : Pour cautiously ~ 110 ml of concentrated H_2SO_4 in thin stream in distilled water with constant stirring and dilute to 1 litre and cool to room temperature.
- NH_4HF_2 / Syrupy H_3PO_4 (85%)
- Barium- (or sodium-) diphenylaminesulphonate (BDS) : Saturated aqueous solution.

Procedure :

- Prepare 250 ml of $\sim(N/20)$ $K_2Cr_2O_7$ solution by accurate weighing.
 $\sim 0.6 - 0.8$ g. of A.R. $K_2Cr_2O_7$ in 250 ml solution.
 $\text{strength} = (w/0.6129) (N/20)$
 where, w = wt. of $K_2Cr_2O_7$ in 250 ml solution.
- Standardisation of Mohr's salt solution.
 Pipette out 25 ml of Mohr's salt solution in a 250 ml conical flask, add 25 ml 4(N) H_2SO_4 , ~ 2 g of NH_4HF_2 (or, 3 ml of syrupy H_3PO_4) and 3-4 drops of BDS indicator. Titrate the solution with the standard $\sim(N/20)$ $K_2Cr_2O_7$ solution till a violet colour appears at the end point. Record the titre (V ml).
- Calculate the strength of Mohr's salt solution in normality and also in g/lit.

Calculation :

Fe^{2+} in 25 ml Mohr's salt solution

$$\equiv V \text{ ml of } (w/0.6129) (N/20) K_2Cr_2O_7$$

∴ Strength of Mohr's salt solution in normality

$$= \left(\frac{V.w}{25 \times 0.6129} \right) (N/20)$$

∴ Equivalent wt. of Mohr's salt = 392.143

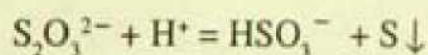
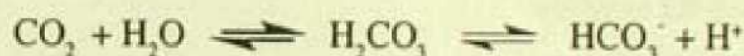
Strength of Mohr's salt solution in g/lit.

$$= \left(\frac{392.143}{25 \times 0.6129 \times 20} \right) (V.w.) \text{ g/lit.}$$

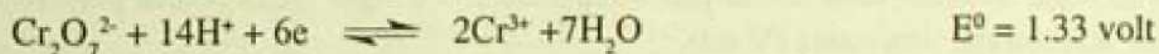
Experiment No. 2 : Standardisation of sodium thiosulfate solution using standard $K_2Cr_2O_7$ solution

Principle :

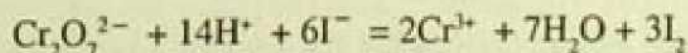
Sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) is not a primary standard substance, because its crystals are efflorescent, its aqueous solution is unstable and turns turbid on standing due to the separation of colloidal sulphur. This may be caused due to acidic action of atmospheric CO_2 , or, by bright sunlight, or, bacteria:



More over, the stoichiometry of direct reaction of $K_2Cr_2O_7$ with thiosulfate is not well defined. For these reasons, thiosulfate solution is to be standardised against a primary standard substance like $K_2Cr_2O_7$ using $I_2 / 2I^-$ redox couple as an intermediate. In acid medium $K_2Cr_2O_7$ quantitatively oxidises KI to I_2 in 2(N) acid medium.



The overall reaction is,



$$[E^0_{\text{cell}} = (1.33 - 0.54) \text{ V} = 0.79 \text{ V} ; \quad K_{298} \sim 10^{80.2}]$$

The liberated I_2 is titrated with the thiosulphate solution in very dilute acid (~ 0.5 N) medium using starch indicator.



$$\therefore [Cr_2O_7^{2-}]/6 \equiv [I^-] \equiv \frac{1}{2} [I_2] \equiv 2[S_2O_3^{2-}]/2 \equiv [S_2O_3^{2-}]$$

or, 1000 ml of (N) $K_2Cr_2O_7 \equiv 1000$ ml of (N) thiosulfate

If V_1 ml S_1 (N) $K_2Cr_2O_7$ solution is equivalent to V_2 ml S_2 (N) thiosulfate solution, then

$$V_1 \times S_1 = V_2 \times S_2$$

Chemicals required :

- Standard (N/20) $K_2Cr_2O_7$ solution : To be prepared by accurate weighing.
- N/20 thiosulfate solution : Dissolve ~ 12.5 g. of A. R. $Na_2S_2O_3 \cdot 5H_2O$ in 500 ml of boiled and cooled distilled water and dilute to 1 litre. Add 2-3 drops of $CHCl_3$ to improve the stability of the solution and store in an amber coloured bottle.
- 4 (N) H_2SO_4 : Pour ~ 110 ml concentrated H_2SO_4 in distilled water and dilute to 1 litre.
- Solid KI / 10% KI solution.
- 1% starch solution.

Procedure :

Pipette out an aliquot of 25 ml standard \sim (N/20) $K_2Cr_2O_7$ solution in a 500 ml conical flask, add 25 ml 4(N) H_2SO_4 , 2 g. of KI. Stopper the flask and keep it in the dark for about 2-3 minutes. Dilute with 150 ml distilled water to adjust the acidity to ~ 0.5 (N) and titrate the liberated I_2 with the thiosulfate solution till a straw yellow colour appears. Add 2 ml of 1% starch indicator. The solution turns intense blue. Continue titration with the thiosulfate solution until the blue colour just disappears and a light green colour persists in the solution. Record the titre value (V ml).

Calculation :

$$\text{Strength of } K_2Cr_2O_7 \text{ solution} = \left(\frac{w}{0.6129} \right) (N/20)$$

where, w = wt. of $K_2Cr_2O_7$ per 250 ml solution.

$$\therefore 25 \text{ ml of } \left(\frac{w}{0.6129} \right) (N/20) K_2Cr_2O_7 \equiv V \text{ ml of thiosulfate solution.}$$

∴ Strength of thiosulfate solution

$$= \left(\frac{25 \times W}{0.6129 \times V} \right) (N/20)$$

Experiment No. 3 : Estimation of Fe^{II}

Principle :

In acid medium Fe^{II} in a solution may be estimated by direct titration with a standard solution of K₂Cr₂O₇ in presence of either phosphoric acid (H₃PO₄) or ammonium bifluoride (NH₄HF₂) using barium diphenylaminesulphonate (BDS) as indicator. Under this condition K₂Cr₂O₇ quantitatively oxidises Fe²⁺ to Fe³⁺:



$$\therefore [\text{Cr}_2\text{O}_7^{2-}]/6 \equiv [\text{Fe}^{2+}]$$

∴ 1000 ml (N) K₂Cr₂O₇ solution \equiv [Fe^{II}] \equiv 55.847g. of Fe \equiv 392.143 g. Mohr's salt

H₃PO₄ (or NH₄HF₂) stabilises Fe³⁺ by complex formation, which is essential for indicator action of BDS.

Chemicals required :

- Standard (N/20) K₂Cr₂O₇ solution : To be prepared by accurate weighing.
- ~N/20 Mohr's Salt solution : Dissolve ~20 g. of A. R. Mohr's salt [(NH₄)₂ SO₄·FeSO₄·6H₂O, F.W. = 392.143] in 500ml of 4(N) H₂SO₄ by heating the solution and then dilute to 1 litre with distilled water.
- 4(N) H₂SO₄ : Pour ~110 ml of concentrated H₂SO₄ in distilled water and dilute to 1 litre.
- Syrupy H₃PO₄ or NH₄HF₂
- Barium diphenylaminesulphonate : Saturated aqueous solution.

Procedure :

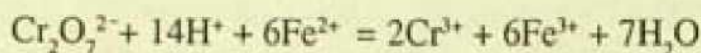
Pipette out 25 ml from the supplied Mohr's salt solution in a 250 ml conical flask. Add 25 ml of 4(N) H₂SO₄, 3 ml of syrupy H₃PO₄ (or, 1-2 g of NH₄HF₂) and 3-4 drops of BDS indicator. Titrate with the standard ~N/20 K₂Cr₂O₇ solution until the colour just changes from green to violet.

Calculate the amount of iron in g/litre in the supplied solution. (See Experiment No. 1)

Experiment No. 4 : Estimation of Fe^{III}

Principle :

To estimate Fe³⁺ present in a solution, it is first reduced to Fe²⁺ either by SnCl₂ or by Zn-amalgam in a Jones reductor or even by highly pure Al-foil in acid medium. Fe²⁺ so obtained is then titrated with standard K₂Cr₂O₇ solution in presence of either phosphoric acid (H₃PO₄) or ammonium bifluoride (NH₄HF₂) using BDS as indicator. The overall reaction is,



$$\therefore [\text{Cr}_2\text{O}_7^{2-}]/6 \equiv [\text{Fe}^{2+}] \equiv [\text{Fe}^{3+}]$$

$$\therefore 1000 \text{ ml (N) K}_2\text{Cr}_2\text{O}_7 \text{ solution} \equiv 55.847 \text{ g of Fe.}$$

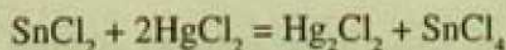
(A) Chemicals Required

- A.R. Hydrochloric acid
- 15% SnCl₂ solution or, Al-foil or Jones reductor
- 5% / 2% HgCl₂ solutions (for SnCl₂ / Jones reductor method)
- Syrupy H₃PO₄/NH₄HF₂
- Barium diphenylaminesulphonate (BDS) indicator solution
- Standard (~ N/20) K₂Cr₂O₇ solution : To be prepared by accurate weighing.
- 4(N) H₂SO₄ solution

Procedure :

1(a). Reduction of Fe³⁺ by SnCl₂ :

Pipette out an aliquot of 25 ml from the supplied Fe^{III} solution in a 500 ml conical flask, add 25 ml conc. HCl, heat nearly to boiling (70 – 90°C) and then add SnCl₂ solution dropwise with constant shaking until the yellow colour of the Fe^{III} solution is just discharged. Add one drop of SnCl₂ in excess. Cool the flask immediately under tap water to room temperature to prevent aerial oxidation of Fe^{II} to Fe^{III}. Add 10 ml 5% HgCl₂ solution *at a time*, shake and allow to stand for about 2-3 minutes, when a slight silky white precipitate of Hg₂Cl₂ appears. This indicates the completeness of reduction of Fe³⁺ to Fe²⁺, since HgCl₂ oxidises excess SnCl₂ if any. HgCl₂ does not oxidise Fe²⁺ to Fe³⁺.



Dilute the solution with ~100 ml of water to maintain the acidity to ~2N. The resulting solution is now ready for titration of Fe^{2+} with $\text{K}_2\text{Cr}_2\text{O}_7$ solution.

(b) *Reduction of Fe^{3+} by A.R. Al-foil :*

Pipette out an aliquot of 25 ml from the supplied Fe^{III} solution in a 500 ml conical flask. Add 25 ml conc. HCl and a few pieces of A.R. Al-foils to the solution. Heat carefully and shake by swirling the flask till the yellow colour of the Fe^{III} solution is discharged (add 1-2 more pieces of A.R. Al-foils if the yellow colour of the solution still persists). Note that the foils are completely disintegrated to give a clear solution.



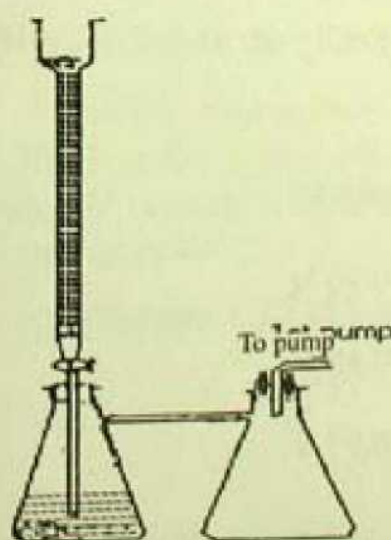
Dilute the solution with ~100 ml of water to maintain the acidity to ~2N. The resulting solution is now ready for titration of Fe^{2+} with $\text{K}_2\text{Cr}_2\text{O}_7$ solution.

(c) *Reduction of Fe^{3+} with Amalgamated Zinc, Zn/Hg (Jones reductor) :*

Amalgamated zinc quantitatively reduces Fe^{3+} to Fe^{2+} .



(i) *Preparation of Amalgamated Zinc column (Jones reductor) :* Cover ~300 g. of A.R. zinc wool, or, pure 20-30 mesh zinc with 2% HgCl_2 solution in a beaker. Add a few drops of HCl, if necessary, to remove the oxide coating from zinc surface. Stir the mixture for about 5-10 minutes and decant off the solution from zinc. Wash three times with water by decantation. The resulting amalgamated zinc should have a bright silvery lustre.



Jones reductor

Take a thin 30-40 cm glass column of internal diameter ~1.5-2 cm having a stop cock with a long stem (15-20 cm) at one end and a ~5 cm cup at the other end. Place a perforated porcelain disc on the groove above the stop cock. Cover with a layer of purified asbestos or glass wool and then fill with amalgamated zinc upto the shoulder of the reductor tube. Wash the amalgamated zinc with ~500 ml distilled water adding in portions using gentle suction.

(ii) *Reduction of Fe^{3+} with Amalgamated Zinc* : At first the amalgamated zinc is to be activated by washing with 50 ml of 2(N) H_2SO_4 keeping the stop cock closed. Place the Jones reductor column on a filtering flask (500 ml / 1litre) using a rubber cork .

Connect the flask to a filtering pump, open the stop cock and percolate the acid solution with gentle suction until the liquid column reaches just above the level of zinc. Close the tap and repeat the process twice. Close the tap and detach the flask. The reductor is now ready for use. It is important to note that during use the level of the liquid should always be just above the zinc column. The solution to be reduced should not contain more than 0.25 g. of Fe^{III} in 100 ml and should be ~2(N) in sulphuric acid.

Pipette out 25 ml from the supplied Fe^{III} solution and pass the same through the reductor using gentle suction. After the solution has passed, wash the column with 100 ml of 2(N) H_2SO_4 in 2-3 portions. The effluent solution is now ready for titration of Fe^{2+} with $K_2Cr_2O_7$ solution. . Wash the column with ~100 ml distilled water and disconnect the column from the suction.

2. *Titration of Fe^{2+} with standard $K_2Cr_2O_7$ solution* :

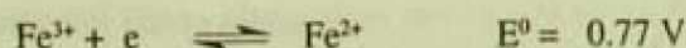
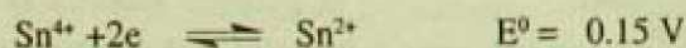
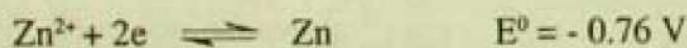
Add 2-3 g. of ammonium bifluoride (or 3 ml of syrupy H_3PO_4) and 4-5 drops of BDS indicator. Titrate with standard ~ (N/20) $K_2Cr_2O_7$ solution until the colour just changes from green to violet.

3. Calculate the amount of iron in g/litre in the supplied solution as usual.

Notes :

Theoretical principle of reduction of Fe^{3+} to Fe^{2+} :

Reduction of Fe^{3+} to Fe^{2+} may be effected by $SnCl_2$, or, Al-foil or Zn/Hg (Jones reductor), all of which are strong reducing agents :



The first three half cells when coupled separately with Fe^{3+}/Fe^{2+} half cell give large E^0_{Cell} values for the respective reactions and hence large values of equilibrium constants.

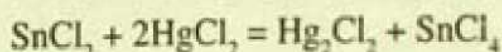
Cell reaction	E^0_{Cell}	$K_{298} = 10^{16.92 n E^0_{\text{Cell}}}$
$2\text{Fe}^{3+} + \text{Sn}^{2+} = 2\text{Fe}^{2+} + \text{Sn}^{4+}$	0.62 V	$\sim 10^{21}$
$2\text{Fe}^{3+} + \text{Zn} = 2\text{Fe}^{2+} + \text{Zn}^{2+}$	1.53 V	$\sim 10^{52}$
$3\text{Fe}^{3+} + \text{Al} = 3\text{Fe}^{2+} + \text{Al}^{3+}$	2.43 V	$\sim 10^{123}$

However, the reaction rate with SnCl_2 solution is slow. The rate can be improved by raising the temperature and maintaining strongly acidic medium, $\sim 5\text{-}6$ (N) HCl . Liberation of hydrogen is prevented during reduction in Jones reductor by increasing the over voltage of hydrogen through amalgamation.

Experiment No. 5 : Estimation of Fe^{II} and Fe^{III} in a mixture

Principle :

In acid medium, direct titration of the $\text{Fe}^{\text{II}} + \text{Fe}^{\text{III}}$ mixture with standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution gives the titre value (V_1) corresponding to the amount of Fe^{2+} . To estimate Fe^{3+} present in the mixture, it is first reduced to Fe^{2+} with just sufficient excess of SnCl_2 in hot 6(N) HCl medium. After cooling the solution to room temperature, the excess SnCl_2 is oxidised by adding HgCl_2 solution when a silky white precipitate of Hg_2Cl_2 appears. This ensures the completeness of reduction of Fe^{3+} to Fe^{2+} and also absence of any excess SnCl_2 .



Acidity of the solution before titration is adjusted to $\sim 2\text{(N)}$ by diluting with distilled water. The resulting solution is then titrated with the same standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution. This titre value (V_2) corresponds to the total iron [$\text{Fe}^{2+} + \text{Fe}^{3+}$]. The difference ($V_2 - V_1$) corresponds to the amount of Fe^{3+} .

In acid medium, $\text{K}_2\text{Cr}_2\text{O}_7$ quantitatively oxidises Fe^{2+} to Fe^{3+} :



$$\therefore [\text{Cr}_2\text{O}_7^{2-}]/6 \equiv [\text{Fe}^{2+}] \equiv [\text{Fe}^{3+}]$$

$$\therefore 1000 \text{ ml of (N) } \text{K}_2\text{Cr}_2\text{O}_7 \text{ solution} \equiv 55.847 \text{ g. of Fe.}$$

Chemicals required :

- 5% HgCl_2 solution.
- 15% SnCl_2 solution.
- NH_4HF_2 / Syrupy H_3PO_4 .
- Barium diphenylaminesulphonate (BDS) indicator solution.
- Standard (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution. To be prepared by accurate weighing.

Procedure :

1. Determination of Fe^{2+} :

Pipette out an aliquot of 25 ml of the $\text{Fe}^{\text{II}} + \text{Fe}^{\text{III}}$ mixture in a 250 ml conical flask, add 25 ml of 4(N) H_2SO_4 , 2 g of NH_4HF_2 (or 3 ml of syrupy H_3PO_4) and 4-5 drops of BDS indicator. Titrate with the standard (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution until the colour of the solution just changes from green to violet. This titre value (V_1) corresponds to Fe^{II} only.

2. Determination of total iron ($\text{Fe}^{2+} + \text{Fe}^{3+}$) :

Pipette out an aliquot of 25 ml of the $\text{Fe}^{\text{II}} + \text{Fe}^{\text{III}}$ mixture in a 500 ml conical flask and add 25 ml conc. HCl . Reduce Fe^{3+} to Fe^{2+} either by Al-foil or by SnCl_2 or by Jones reductor according to the procedures described earlier. (cf. Experiment - 4)

Dilute the solution to 100 ml with distilled water to adjust 2(N) acidity, add ~2 g of NH_4HF_2 (or 5 ml of syrupy H_3PO_4) and 4-5 drops of BDS indicator. Titrate the solution with the same standard (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution until the colour changes from green to violet. This titre value (V_2) corresponds to total iron ($\text{Fe}^{2+} + \text{Fe}^{3+}$) and the difference ($V_2 - V_1$) gives the amount of Fe^{III} .

3. Calculate the amount of Fe^{II} and Fe^{III} present in the sample solution.

Calculation :

$$\text{Fe}^{\text{II}} \text{ in 25 ml solution} = V_1 \text{ ml of } \left(\frac{w}{0.6129} \right) (\text{N/20}) \text{K}_2\text{Cr}_2\text{O}_7$$

$$\text{Fe}^{\text{III}} \text{ in 25 ml solution} = (V_2 - V_1) \text{ ml of } \left(\frac{w}{0.6129} \right) (\text{N/20}) \text{K}_2\text{Cr}_2\text{O}_7$$

where, w = wt. of $\text{K}_2\text{Cr}_2\text{O}_7$ in 250 ml solution.

$$\therefore 1000 \text{ ml of (N) K}_2\text{Cr}_2\text{O}_7 \equiv 55.847 \text{ g. of Fe}$$

$$\equiv 1000 \text{ ml of (N) Fe}$$

∴ Strength of the solution will be :

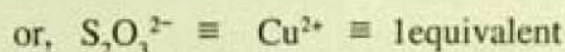
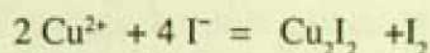
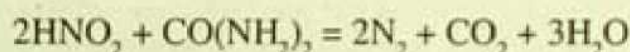
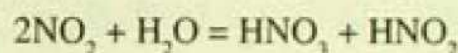
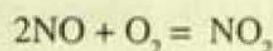
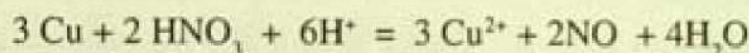
$$[\text{Fe}^{\text{II}}] = \left(\frac{V_1 \cdot w}{25 \times 0.6129} \right) (N/20) = \left(\frac{55.847}{25 \times 0.6129 \times 20} \right) \cdot (V_1 \cdot w) \text{ g/lit.}$$

$$[\text{Fe}^{\text{III}}] = \left(\frac{(V_2 - V_1) \cdot w}{25 \times 0.6129} \right) (N/20) = \left(\frac{55.847}{25 \times 0.6129 \times 20} \right) \cdot [(V_2 - V_1) \cdot w] \text{ g/lit.}$$

Experiment No. 6 : Estimation of Cu in Brass

Principle :

A weighed quantity of brass is dissolved in (1:1) nitric acid and nitrous fumes are removed by boiling with urea. Copper is then iodometrically estimated by treating the solution containing Cu^{2+} with an excess of KI solution, when sparingly soluble cuprous iodide, (Cu_2I_2), is precipitated with liberation of equivalent amount of iodine. Copper is estimated by titrating the liberated iodine with a standard solution of sodium thiosulfate.



∴ 1000 ml of (N) thiosulfate solution \equiv 63.546 g. of Cu

Chemicals required :

- Brass alloy
- Standard (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution : To be prepared by accurate weighing.

- c) $\sim(N/20)$ $\text{Na}_2\text{S}_2\text{O}_3$ solution : Dissolve about ~ 25 g. of A.R. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in 500 ml recently boiled and cooled distilled water and dilute to 1 litre.
- d) Solid KI or 10% KI solution.
- e) 1% Starch solution.
- f) Urea (A.R.)

Procedure :

1. Standardisation of sodium thiosulfate solution :

Follow the procedure described before (cf. Experiment No. 2).

2. Dissolution of Brass :

Weigh out accurately about 1.0 g of the supplied brass into a 250 ml beaker and add 10 ml of distilled water followed by 10 ml of concentrated nitric acid successively down the side of the beaker. Cover the beaker with a clock glass and heat carefully on an asbestos board over a low flame until dissolution is complete. Dilute with 25 ml of water and boil for 5 minutes with 1 g. of urea. Allow it to cool to room temperature. Transfer the solution quantitatively from the beaker in to a 250 ml volumetric flask by washing with distilled water and finally make up the volume up to the mark with distilled water. Mix uniformly (stock solution).

3. Estimation of Cu^{2+} :

Pipette out 25 ml from the above stock solution in a 500 ml conical flask, dilute to 50 ml with distilled water. Neutralise with 1:1 aqueous NH_3 adding dropwise with stirring until a permanent light blue turbidity appears (avoid excess ammonia). Add 2 g. of NH_4HF_2 and shake to obtain a clear solution. Add 10 ml of 10% KI solution and titrate the liberated I_2 immediately with the standardised $\sim(N/20)$ thiosulfate solution adding the starch indicator near the end point. Continue the addition of thiosulfate solution till the milky white precipitate of Cu_2I_2 is visible at the end point.

4. Calculate the % of Cu present in the supplied sample of brass.

Notes :

- (i) The optimum pH for the determination of copper by iodometric method is $\sim 3-4$.
- (ii) In this iodometric determination of copper, some amount of iodine may be adsorbed by the precipitate of Cu_2I_2 . To release this iodine, small amount of ammonium thiocyanate

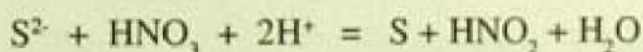
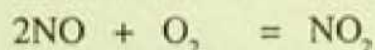
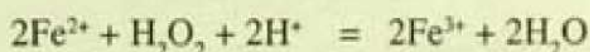
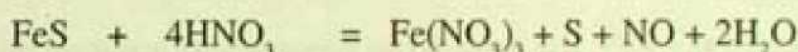
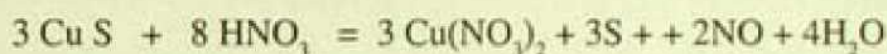
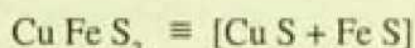
may be added near the end point (i.e., when the blue colour of the starch-iodine adsorption complex fades) and then the titration is completed as quickly as possible to minimize aerial oxidation. At the end point the precipitate attains a pale pink shade.

- (iii) E° value of $I_2/2I^-$ couple (0.54 v) is higher than that of the Cu^{2+}/Cu^+ couple (0.15 v). Yet, Cu^{2+} quantitatively oxidises iodide to iodine, since the formal potential of Cu^{2+}/Cu^+ couple is increased sufficiently above the E° value of $I_2/2I^-$ couple, as the Cu^+ ions disappear from the system due to precipitation of sparingly soluble Cu_2I_2 .

Experiment No. 7 : Estimation of Cu in Chalcopyrites

Principle :

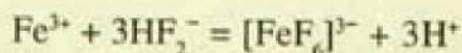
The sulphide ore of copper, $CuFeS_2$ is known as *chalcopyrites*. It is dissolved in HNO_3 when some sulfur is separated. The mixture is then gently warmed with "20 Volume" H_2O_2 to complete the oxidation of Fe^{II} to Fe^{III} , the excess H_2O_2 is then decomposed by boiling. Nitrous fumes are removed by boiling with urea.



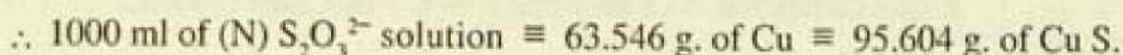
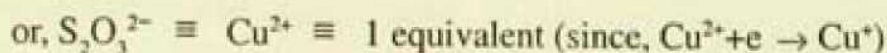
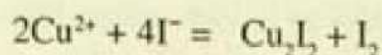
The resultings solution will contain Fe^{3+} and Cu^{2+} as their nitrates.

Both Fe^{3+} and Cu^{2+} liberate I_2 from KI solution*, but Cu^{2+} can be estimated from the mixture by complexing Fe^{3+} as $[FeF_6]^{3-}$ by adding NH_4HF_2 . Due to this complex formation the formal potential of Fe^{3+}/Fe^{2+} system falls below standard reduction potential (E°) of $\frac{1}{2} I_2 / I^-$ system. As a result, Fe^{3+} cannot oxidise I^- to I_2 in presence of F^- .

* E° values of Fe^{3+}/Fe^{2+} , Cu^{2+}/Cu^+ and $I_2/2I^-$ couples are 0.77, 0.15 and 0.54 volt. respectively.



But Cu^{2+} does not form any stable complex with F^- and quantitatively oxidises I^- to I_2 and the liberated I_2 is titrated with a standard thiosulfate solution using starch as indicator.



(B) Chemicals required :

- Chalcopyrites.
- HNO_3 (A.R.)
- 20 volume H_2O_2
- 1 : 1 NH_3 solution
- NH_4HF_2
- 10% KI solution
- Standard (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution. To be prepared by accurate weighing.
- ~ (N/20) sodium thiosulfate solution
- 1% starch solution
- Ammonium thiocyanate

Procedure :

1. Dissolution of Chalcopyrites :

Attack ~ 1.0 g of the powdered chalcopyrites with a mixture of 10 ml of water and 3 ml of conc. HNO_3 , heat gently on an asbestos board till dissolution of the ore is complete. Add water to replenish the loss of volume of the solution due to evaporation. The elemental sulfur that is set free remains suspended in the solution. Dilute the solution with 50 ml of water, cool to room temperature and remove the sulfur particles by filtration (or, with the help of a glass rod if a globule is formed). Add 10 ml of "20 Volume" H_2O_2 and warm gently to complete the oxidation of Fe^{2+} to Fe^{3+} , boil for about 10 minutes to decompose the excess H_2O_2 . Cool to room temperature. Filter if necessary and transfer quantitatively into a 100 ml volumetric flask and make up to the mark with distilled water.

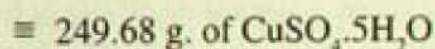
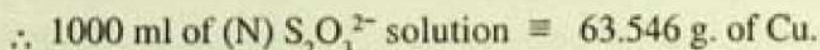
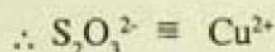
2. Estimation of Cu^{2+} :

- (i) Standardise the the ($\sim \text{N}/20$) thiosulfate solution against the standard ($\text{N}/20$) $\text{K}_2\text{Cr}_2\text{O}_7$ solution following the usual procedure (cf. Experiment No. 2)
 - (ii) Pipette out 25 ml of the diluted solution into a 500 ml conical flask and remove the nitrous fumes by boiling with 1 g of urea, dilute to 100 ml with water, neutralise with (1: 1) NH_3 to obtain a permanent turbidity (avoid excess NH_3) and dissolve the same by adding 2-3 g. of NH_4HF_2 . Add 10 ml of 10% KI solution and titrate the liberated I_2 with standard ($\text{N}/20$) thiosulfate solution adding 2 ml of 1% starch solution near the end point. Continue the titration till a milky white end point is attained. (Add 1 g. of ammonium thiocyanate near the end point, shake well and complete the titration).
3. Calculate the % of Cu and CuS in the sample of chalcopyrites.

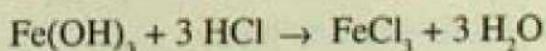
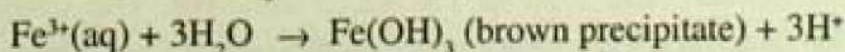
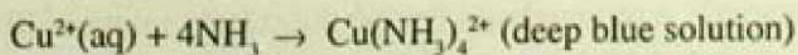
Experiment No. 8 : Estimation of Fe^{III} and Cu^{II} in Mixture

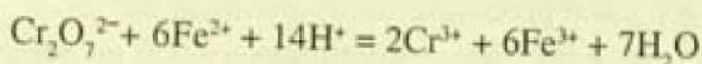
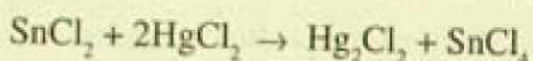
Principle :

Both Fe^{3+} and Cu^{2+} can liberate I_2 from KI solution, but Cu^{2+} can be iodometrically estimated from the mixture by complexing Fe^{3+} as $[\text{FeF}_6]^{3-}$ by adding NH_4HF_2 .

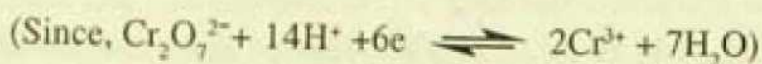


To estimate iron in the mixture, Fe^{3+} is first precipitated as hydrated ferric oxide, by adding aqueous ammonia. It is filtered and washed free from copper then dissolved in hot 6(N) HCl, reduced to Fe^{2+} by SnCl_2 method or with Al-foil and Fe^{2+} so obtained is estimated by titrating with standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution using barium diphenylaminesulphonate as indicator, in presence of NH_4HF_2 or H_3PO_4 .





$\therefore (1/6) \text{K}_2\text{Cr}_2\text{O}_7 \equiv \text{Fe}^{2+} \equiv 1 \text{ equivalent} \equiv 55.847 \text{ g. of Fe.}$



$\therefore 1000 \text{ ml of (N) } \text{Cr}_2\text{O}_7^{2-} \text{ solution} \equiv 55.847 \text{ g. of Fe}$

Chemicals required :

- 15% SnCl_2 solution or, Al-foil
- 5% HgCl_2 solution (if SnCl_2 solution is used)
- Syrupy $\text{H}_3\text{PO}_4 / \text{NH}_4\text{HF}_2$
- Barium diphenylaminesulphonate (BDS) indicator solution
- Standard (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution, to be prepared by accurate weighing.
- ~(N/20) sodium thiosulfate solution : Dissolve about ~25 g. of A.R.

$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in 500 ml recently boiled and cooled distilled water and dilute to 1 litre.

- 10% KI solution.
- 1% starch solution.

Procedure :

- Preparation of 250 ml of a standard (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution by accurate weighing.
- Standardisation of sodium thiosulfate solution. (cf. Experiment No. 2).
- Estimation of Cu^{2+} :*

Pipette out 25 ml of the prepared solution into a 500 ml conical flask, dilute to 100 ml with water, neutralise with 1:1 aqueous NH_3 to obtain a permanent turbidity (avoid excess NH_3) and dissolve the same by adding 2 g. of NH_4HF_2 . Add 10 ml of 10% KI and titrate the liberated I_2 with standard ~ (N/20) thiosulfate solution till the solution assumes a straw yellow colour. Add 2 ml of 1% starch indicator. The solution turns intense blue. Continue the titration till the milky white precipitate of Cu_2I_2 appears. Record the titre and calculate the amount of copper in the sample solution.

4. Estimation of Fe^{3+} :

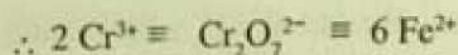
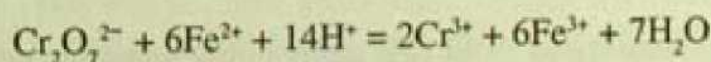
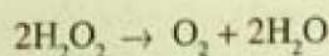
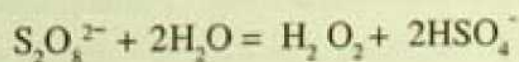
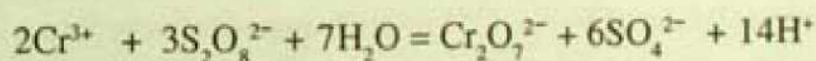
Pipette out 25 ml of the prepared solution, dilute to 100 ml with distilled water, add 1g. of A.R. NH_4Cl , warm and add 1:1 aqueous ammonia to precipitate ferric hydroxide. Filter the precipitate using a Whatman No. 41 filter paper and wash 2-3 times with 1% NH_4Cl solution containing a little NH_3 . Dissolve the precipitate in minimum volume of hot (1:2) HCl , reprecipitate with 1:1 aqueous ammonia and refilter through the same filter paper, and wash as before till the washings are colourless. Dissolve the precipitate in 50 ml of hot 6(N) HCl . Introduce a few pieces of A.R. Al-foil and swirl the solution till the reduction of Fe^{3+} is complete and the foils disintegrate and dissolve completely, giving a clear solution. Cool the solution quickly to room temperature. Dilute to 150 ml with distilled water to adjust the acidity to ~2(N). Add 2-3 g. of NH_4HF_2 , 4 - 5 drops of BDS indicator and titrate the solution with the standard (N/20) $K_2Cr_2O_7$ solution to a violet end point. Record the titre and calculate the amount of iron in the sample solution.

Note : Iodometric estimation of copper in $CuSO_4 \cdot 5H_2O$ solution can be carried out by the same procedure, involving (i) Standardization of (~N/20) thiosulfate solution against standard (N/20) $K_2Cr_2O_7$ solution (cf. Experiment No. 2) and (ii) Estimation of Cu (Experiment Nos 7, 8).

Experiment No. 9 : Estimation of Fe^{III} and Cr^{III} in Mixture

Principle :

Chromium (III) present in the mixture is first oxidised to dichromate ($Cr_2O_7^{2-}$) by boiling with an excess of ammonium/potassium peroxydisulphate in presence of a small amount of $AgNO_3$ as catalyst. The unreacted peroxydisulphate is then decomposed by boiling. The dichromate so produced is estimated by adding a measured excess of standard Mohr's salt solution and then back titrating of the excess Mohr with a standard $K_2Cr_2O_7$ solution using barium diphenylaminesulphonate as indicator in presence of H_3PO_4 or NH_4HF_2 .



$$\therefore \text{Fe}^{2+} \equiv (1/6) \text{K}_2\text{Cr}_2\text{O}_7 \equiv (1/3) \text{Cr}^{3+} \equiv 1 \text{ equivalent}$$

$$\begin{aligned} \therefore 1000 \text{ ml of (N) Mohr's salt solution} &\equiv 1000 \text{ ml of (N) K}_2\text{Cr}_2\text{O}_7 \\ &\equiv 49.03 \text{ g. of K}_2\text{Cr}_2\text{O}_7 \\ &\equiv 51.996/3, \text{ or, } 17.332 \text{ g. of Cr} \end{aligned}$$

For the estimation of iron, the solution oxidised with ammonium peroxydisulphate is to be treated with 1:1 aqueous ammonia to precipitate Fe^{III} as ferric hydroxide, which is filtered, washed free from $\text{Cr}_2\text{O}_7^{2-}$. It is then dissolved in hot 6(N) HCl. Fe^{3+} is then reduced to Fe^{2+} by Al-foil or by SnCl_2 method and finally estimated by titrating with standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution using barium diphenylaminesulphonate as indicator in presence of H_3PO_4 or NH_4HF_2



$$\therefore \frac{\text{Cr}_2\text{O}_7^{2-}}{6} \equiv \text{Fe}^{2+}$$

$$1000 \text{ ml of (N) Cr}_2\text{O}_7^{2-} \equiv 55.847 \text{ g. of Fe}$$

Chemicals required :

- 15% SnCl_2 solution or, Al-foil
- 5% HgCl_2 solution (if SnCl_2 is used).
- Syrupy H_3PO_4 or NH_4HF_2
- Barium diphenylaminesulphonate (BDS) indicator
- 0.1(M) AgNO_3 solution.

Procedure :

1. Prepare 250 ml of a standard (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution by accurate weighing.
2. Standardisation of ~N/20 Mohr's salt solution. (cf. Experiment No. 1).
3. Transfer the supplied solution of $\text{Fe}^{\text{III}} + \text{Cr}^{\text{III}}$ mixture quantitatively into a 250 volumetric flask and make up to the mark with distilled water. (Acidity should be ~ 2N).

4. Estimation of Cr :

Pipette out 25 ml from the above diluted stock solution in a 500 ml conical flask, add 20 ml of 0.1(M) AgNO_3 solution and 50 ml 10% ammonium/potassium peroxydisulphate solution. Then carefully add 8 ml of conc. H_2SO_4 with stirring, cover the flask with a clock

glass and boil gently for about 20 minutes. The solution has assumes an orange colour. Allow the solution to cool, dilute to 150 ml with distilled water and add a measured excess (25/50/75 ml say $(25 \times x)$ ml) of standard (N/20) Mohr's salt solution with a pipette or a burette to discharge the orange colour due to $\text{Cr}_2\text{O}_7^{2-}$. Add 5 ml of syrupy H_3PO_4 (or 2 g. of NH_4HF_2) and 4-5 drops of BDS indicator. Titrate the solution with the standard (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution to a violet end point. The amount of Cr is obtained from the difference in the titre values.

Calculation :

Let V ml of sample chromium solution is oxidised to dichromate ($\text{Cr}_2\text{O}_7^{2-}$)

If 25 ml (N/20) Mohr solution $\equiv V_1$ ml of f.(N/20) $\text{K}_2\text{Cr}_2\text{O}_7$

and $25 \times x$ ml of the same (N/20) Mohr solution

$\equiv V_2$ ml f.(N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ + oxidised sample chromium solution

Then, oxidised sample chromium solution $\equiv (V_1 \times x - V_2)$ ml of f.(N/20) $\text{K}_2\text{Cr}_2\text{O}_7$.

\therefore Total volume of sample solution is 250 ml

$$\therefore \text{Total Cr in 250 ml} = \frac{17.332 \times (V_1 x - V_2) f \times 250}{1000 \times 20 \times V} \text{ g.} = 0.2167 \times f \times \left(\frac{V_1 x - V_2}{V} \right) \text{ g.}$$

where, f = factor of standard (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution

$$= \frac{\text{wt. of } \text{K}_2\text{Cr}_2\text{O}_7 \text{ in 250 ml solution (w)}}{0.6129}$$

$$\therefore \text{Total Cr in 250 ml sample solution} = 0.3535 \times \frac{w (V_1 x - V_2)}{V} \text{ g.}$$

4. Estimation of Fe^{3+} :

Pipette out 25 ml of the diluted stock solution and oxidise Cr^{3+} to $\text{Cr}_2\text{O}_7^{2-}$ as before. Cool the solution, dilute to 100 ml with distilled water, add 1g. of A.R. NH_4Cl , warm and add 1:1 aqueous NH_3 till ammoniacal to precipitate ferric hydroxide completely. Allow the precipitate to settle, then filter through a Whatman No. 41 filter paper and wash 2-3 times with 1% NH_4Cl solution containing a little NH_3 . Discard the filtrate and the washings. Dissolve the precipitate in minimum volume of hot dil. (1:2) HCl , reprecipitate with 1:1

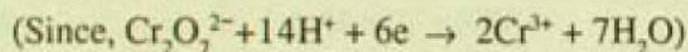
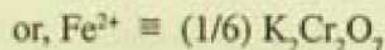
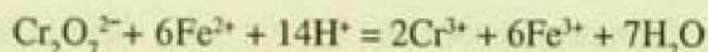
aqueous NH_3 , refilter using the same filter paper, and wash as before till the washings are colourless. Dissolve the precipitate in 50 ml of hot 6(N) HCl and reduce Fe^{III} with Al -foil as usual. Dilute to 150 ml with distilled water to adjust the acidity to $\sim 2(\text{N})$, add 2.0 g. of NH_4HF_2 (or, 5 ml of syrupy H_3PO_4), 4 - 5 drops of BDS indicator and titrate with standard (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution to a violet end point. Record the titre and calculate the amount of iron present in the sample solution using the equivalence :

$$1000 \text{ ml of (N) } \text{K}_2\text{Cr}_2\text{O}_7 \equiv \text{Fe} \equiv 55.847 \text{ g. of Fe. (cf. Experiment No. 5)}$$

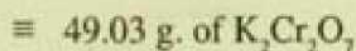
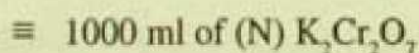
Experiment No. 10 : Estimation of Fe^{III} - $\text{Cr}_2\text{O}_7^{2-}$ in Mixture

Principle :

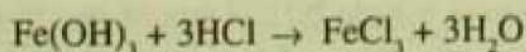
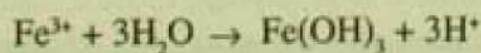
$\text{Cr}_2\text{O}_7^{2-}$ is directly estimated in presence of Fe^{3+} by adding measured excess of standard Mohr's salt solution and then back titrating the excess Mohr with standard $\text{Cr}_2\text{O}_7^{2-}$ solution using barium diphenylaminesulphonate as indicator in presence of H_3PO_4 or NH_4HF_2 .

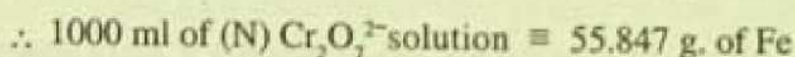
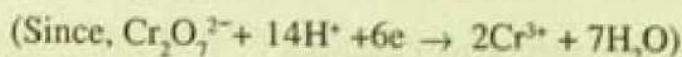
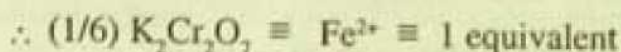
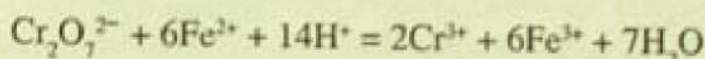
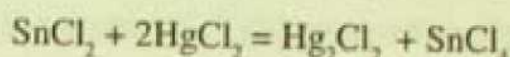
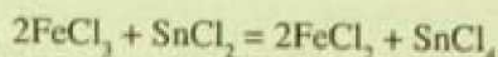


\therefore 1000 ml of (N) Mohr's salt solution



For estimation of Fe^{3+} , it is first precipitated as ferric hydroxide, by treating the solution with aqueous ammonia. After filtration and washing, the precipitated hydroxide is dissolved in hot 6(N) HCl . Fe^{3+} is then reduced to Fe^{2+} by Al - foil or by SnCl_2 method. Finally Fe^{2+} is estimated by titrating with standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution using BDS as indicator in presence of H_3PO_4 or NH_4HF_2 .





Chemicals required :

- 1) 15% SnCl_2 solution, or, Al-foil.
- 2) 5% HgCl_2 solution (if SnCl_2 is used).
- 3) NH_4HF_2 or Syrupy H_3PO_4 .
- 4) Barium diphenylaminesulphonate (BDS) indicator.

Procedure :

1. Prepare a standard (N/20) potassium dichromate solution in a 250 ml volumetric flask by accurate weighing.

2. *Standardisation of Mohr's salt solution:*

Pipette out an aliquot of 25 ml Mohr's salt solution in a 500 ml conical flask, add 25 ml of 4(N) H_2SO_4 , 2 g. of NH_4HF_2 or 3 ml of syrupy H_3PO_4 and 3-4 drops of barium diphenylaminesulphonate indicator. Titrate the solution with the standard (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution to a violet end point.

3. *Estimation of $\text{Cr}_2\text{O}_7^{2-}$:*

Pipette out an aliquot of 25 ml from the prepared solution in a 500 ml conical flask, add a measured excess (25/50/75 ml) of standard ~ (N/20) Mohr's salt solution to discharge the dichromate colour. Dilute to 150 ml with 2(N) H_2SO_4 , add 2g. of NH_4HF_2 (or, 5 ml of syrupy H_3PO_4) and 3-4 drops of BDS indicator. Titrate the solution with the standard (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution to a violet end point. The amount of $\text{Cr}_2\text{O}_7^{2-}$ is obtained from the difference in the titre values.

Calculation :

Let, V ml of sample dichromate ($\text{Cr}_2\text{O}_7^{2-}$) solution is treated with $(25 \times x)$ ml of Mohr's salt solution.

If 25 ml of (N/20) Mohr's solution

$$\equiv V_1 \text{ ml of } f.(N/20) \text{ K}_2\text{Cr}_2\text{O}_7 \text{ solution,}$$

$\therefore (25 \times x)$ ml of (N/20) Mohr's solution

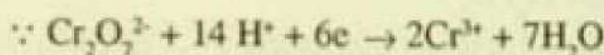
$$\equiv V_2 \text{ ml of } f.(N/20) \text{ K}_2\text{Cr}_2\text{O}_7 \text{ solution} + V \text{ ml of sample } \text{Cr}_2\text{O}_7^{2-}$$

$\therefore V$ ml of sample $\text{Cr}_2\text{O}_7^{2-}$ solution

$$\equiv (V_1 x - V_2) \text{ ml of } f.(N/20) \text{ K}_2\text{Cr}_2\text{O}_7$$

Since the total volume of sample solution is 250 ml

$$\therefore \text{Total } \text{Cr}_2\text{O}_7^{2-} \text{ in 250 ml} \equiv \frac{(V_1 x - V_2)}{V} \times 250 \text{ ml of } f.(N/20) \text{ K}_2\text{Cr}_2\text{O}_7$$



$$\therefore 1 \text{ Equivalent of } \text{Cr}_2\text{O}_7^{2-} \equiv \frac{\text{Cr}_2\text{O}_7^{2-}}{6}$$

$$\equiv \frac{215.988}{6} \text{ g. of } \text{Cr}_2\text{O}_7^{2-} = 36 \text{ g. of } \text{Cr}_2\text{O}_7^{2-}$$

$$\therefore 1000 \text{ ml of (N) } \text{Cr}_2\text{O}_7^{2-} \equiv 36 \text{ g. of } \text{Cr}_2\text{O}_7^{2-}$$

$$\therefore \left(\frac{(V_1 x - V_2) 250}{V} \right) \text{ ml of } f.(N/20) \text{ K}_2\text{Cr}_2\text{O}_7 \equiv \left[\left(\frac{36 \times 250}{1000 \times 20} \right) \right] f. \left(\frac{V_1 x - V_2}{V} \right) \text{ g. of } \text{Cr}_2\text{O}_7^{2-}$$

$$= 0.45 f \left(\frac{V_1 x - V_2}{V} \right) \text{ g. of } \text{Cr}_2\text{O}_7^{2-}$$

$$\text{where, } f = \frac{\text{wt. of } \text{K}_2\text{Cr}_2\text{O}_7 \text{ in 250 ml (w)}}{0.6129}$$

$$\therefore \text{Total } \text{Cr}_2\text{O}_7^{2-} \text{ in 250 ml} = 0.7342 \times \frac{w (V_1 x - V_2)}{V} \text{ g.}$$

4. Estimation of Fe :

Pipette out 25 ml of the supplied mixture in a 500 ml conical flask, dilute to 100 ml with distilled water, add 1g. of A.R. NH_4Cl , heat nearly to boiling and add (1:1) aqueous

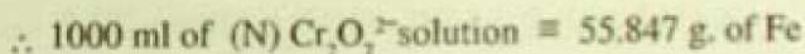
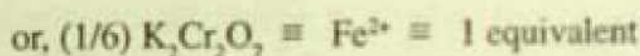
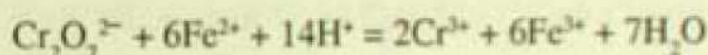
NH_3 till ammoniacal to precipitate ferric hydroxide completely. Allow the precipitate to settle and then filter it through a Whatman No. 41 filter paper and wash the precipitate 2-3 times with 1% NH_4Cl solution containing a little NH_3 . Dissolve the precipitate in minimum volume of hot dilute (1:2) HCl , reprecipitate with 1:1 aqueous NH_3 and refilter through the same filter paper and wash as before till the washings are colourless. Dissolve the precipitate in 50 ml of hot 6(N) HCl and reduce Fe^{3+} to Fe^{2+} by Al-foil as usual. Dilute to 150 ml with distilled water to adjust the acidity to 2(N), add 2 g. of NH_4HF_2 (or, 5 ml of syrupy H_3PO_4), 4-5 drops of BDS indicator and titrate with standard (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution to a violet end point. Record the titre value. Calculate the amount of iron present in the sample solution (cf. Experiment No. 5).

Experiment No. 11 : Estimation of Fe and Mn in Mixture

Principle :

Estimation of Fe

If iron is present in Fe^{III} state, it has to be reduced to Fe^{II} state by Al-foil or by SnCl_2 method, the resulting Fe^{II} is then estimated by titrating with the standard $\text{Cr}_2\text{O}_7^{2-}$ solution using BDS indicator in presence of H_3PO_4 or NH_4HF_2 .

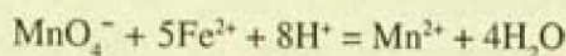


Estimation of Mn

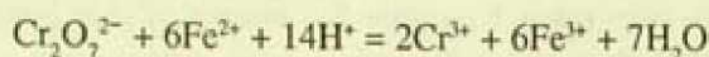
(a) Bismuthate oxidation method :

Mn^{2+} is oxidised to MnO_4^- with sodium bismuthate (NaBiO_3) and the resulting permanganate after separation from excess oxidant by filtration, is treated with a measured excess of standard Mohr's salt solution. The excess Mohr is then back titrated with a standard

$\text{Cr}_2\text{O}_7^{2-}$ solution using BDS as indicator in presence of H_3PO_4 or NH_4HF_2 . The amount of Mn is obtained from the difference in the titre values.



$$\therefore \frac{\text{MnO}_4^-}{5} \equiv \frac{\text{Mn}}{5} \equiv \text{Fe}$$



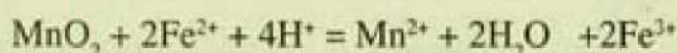
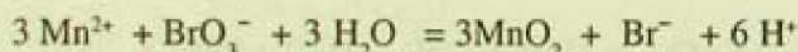
$$\therefore \frac{\text{Cr}_2\text{O}_7^{2-}}{6} \equiv \text{Fe}$$

$$\therefore \frac{\text{Cr}_2\text{O}_7^{2-}}{6} \equiv \text{Fe} \equiv \frac{\text{MnO}_4^-}{5} \equiv \frac{\text{Mn}}{5} \equiv \frac{55.938}{5} \text{ g. of Mn}$$

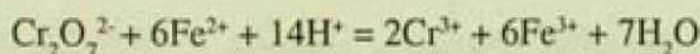
$$\therefore 1000 \text{ ml (N) } \text{K}_2\text{Cr}_2\text{O}_7 \equiv 11.1876 \text{ g. of Mn}$$

(b) Bromate oxidation method :

Mn^{2+} is oxidised to MnO_2 by boiling with potassium bromate (KBrO_3) in dil H_2SO_4 medium. Precipitated MnO_2 is filtered, washed free from the excess oxidant and then dissolved in a measured excess of standard Mohr's salt solution, when MnO_2 is reduced to Mn^{2+} . The excess Mohr is then back titrated with a standard $\text{Cr}_2\text{O}_7^{2-}$ solution in presence of phosphoric acid, or NH_4HF_2 using BDS as indicator. Amount of Mn is obtained from the difference in the titre values.



$$\frac{\text{MnO}_2}{2} \equiv \frac{\text{Mn}}{2} \equiv \text{Fe}$$



$$\therefore \frac{\text{Cr}_2\text{O}_7^{2-}}{6} \equiv \text{Fe}$$

$$\therefore \frac{\text{Cr}_2\text{O}_7^{2-}}{6} \equiv \text{Fe} \equiv \frac{\text{MnO}_2}{2} \equiv \frac{\text{Mn}}{2} \equiv \frac{54.94}{2} \text{ g. of Mn} = 27.47 \text{ g. of Mn}$$

$$\therefore 1000 \text{ ml of (N) } \text{K}_2\text{Cr}_2\text{O}_7 \equiv 27.47 \text{ g. of Mn}$$

(The result has to be multiplied by an empirical factor of 1.01 to obtain the accurate amount).

Chemicals and Equipment required

- a) HCl (A.R.)
- b) Al-foil
- c) Syrupy H_3PO_4 or, NH_4HF_2
- d) Barium diphenylaminesulphonate (BDS) indicator
- e) H_2SO_4 (A.R.)
- f) Sodium bismuthate (A.R.)
- g) $\sim (\text{N}/20)$ Mohr's salt solution
- h) 5% (A.R.) KBrO_3 solution
- i) Asbestos pulp filter / sintered glass crucible.
- j) Suction filtering system.
- k) Whatman No. 41 filter paper

Procedure :

1. Prepare 250 ml a standard (N/20) potassium dichromate solution by accurate weighing. Standardize the ($\sim \text{N}/20$) Mohr's salt solution against the standard (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution (cf. Experiment No. 1).

2. *Estimation of Fe :*

Pipette out 25 ml of the stock solution in a 500 ml conical flask and acidify with 25 ml of conc. HCl. Heat just to boiling and reduce Fe^{3+} ion with Al-foil as usual. Dilute to 150 ml with water to adjust acidity $\sim 2(\text{N})$. Add 2 g. of NH_4HF_2 (or, 5 ml of syrupy H_3PO_4) and 3-4 drops of BDS indicator. Titrate with the standard (N/20) $\text{Cr}_2\text{O}_7^{2-}$ solution to a violet end point.

3.(a) *Estimation of Mn by bismuthate oxidation method :*

Pipette out 25 ml of the stock solution in a 250 ml beaker, add 10 ml conc. H_2SO_4 dilute to 100 ml (to adjust $\sim 3(\text{N})$ acidity) and allow to cool room temperature. Oxidise with about 0.5 g. of sodium bismuthate. Filter through a sintered-glass crucible or through an asbestos pulp bed fitted with a suction pump. Wash with 2(N) H_2SO_4 till the washings are colourless.

To the combined filtrate and washings, add a measured excess, (25/50/75, say $(25 \times x)$ ml) of standard $\sim (\text{N}/20)$ Mohr's salt solution to discharge the permanganate colour. Add 2.0 g. of NH_4HF_2 (or, 5 ml of syrupy H_3PO_4) and 4-5 drops of BDS indicator. Back titrate the excess Mohr with the same standard (N/20) $\text{Cr}_2\text{O}_7^{2-}$ solution to a violet end point. Calculate the amount of Mn from the difference in the titre values.

(b) *Estimation of Mn by bromate oxidation method :*

Pipette out 25 ml of the stock solution in a 250 ml conical flask. Add 10 ml of 4(N) H_2SO_4 to adjust the acidity to $\sim 1(\text{N})$ and then add 10 ml of 5% KBrO_3 solution. Cover the flask with a clock glass and heat the mixture to gentle boiling for 15 to 20 minutes with occasional addition of water to make up for the reduction in volume due to evaporation. Allow the mixture to cool to room temperature. Filter the precipitated MnO_2 through a Whatman No. 41 filter paper. If the filtrate is turbid, refilter the first portion of the filtrate through the same filter paper. Wash with hot water, using 5 ml portion each time, till the washings are free from BrO_3^- (test with starch-KI in acidic medium).

Transfer the brown precipitate of MnO_2 along with the filter paper into the original conical flask, add 25 ml of 4(N) H_2SO_4 and a measured excess (25/50/75, say $(25 \times x)$ ml) of standard ($\sim \text{N}/20$) Mohr's salt solution using a pipette or a burette and stir the mixture to completely dissolve the precipitate of MnO_2 . Add 2-3 g. of NH_4HF_2 (or, 5 ml of syrupy H_3PO_4) and 4-5 drops of BDS indicator. Back titrate the excess Mohr with the standard ($\text{N}/20$) $\text{K}_2\text{Cr}_2\text{O}_7$ solution to a violet end point. Calculate the amount of Mn from the difference in the titre values.

Calculation :

(a). Bismuthate oxidation method :

Let V ml of sample Mn solution is oxidised to MnO_4^-

If 25 ml of ($\sim \text{N}/20$) Mohr's solution $\equiv V_1$ ml of $f.(\text{N}/20) \text{K}_2\text{Cr}_2\text{O}_7$

and $(25 \times x)$ ml ($\text{N}/20$) Mohr's solution

$\equiv V_2$ ml of $f.(\text{N}/20) \text{K}_2\text{Cr}_2\text{O}_7 + \text{MnO}_4^-$ obtained from V ml of sample Mn solution

$\therefore \text{MnO}_4^-$ in V ml of sample Mn solution $\equiv (V_1 x - V_2)$ ml of $f.(\text{N}/20) \text{K}_2\text{Cr}_2\text{O}_7$

$\therefore 1000$ ml of (N) $\text{K}_2\text{Cr}_2\text{O}_7 \equiv 11.1876$ g. of Mn

$\therefore (V_1 x - V_2)$ ml of $f.(\text{N}/20) \text{K}_2\text{Cr}_2\text{O}_7 \equiv \frac{11.1876 \times (V_1 x - V_2) \times f}{1000 \times 20}$ g. of Mn

Since the volume of the sample solution oxidised = V ml and total volume of the sample solution is 250 ml,

$$\begin{aligned} \therefore \text{Total Mn in 250 ml} &= \frac{11.1876 \times (V_1 x - V_2) \times f \times 250}{1000 \times 20 \times V} \text{ g.} \\ &\approx 0.14 \times f \times \left(\frac{V_1 x - V_2}{V} \right) \text{ g.} \end{aligned}$$

where, f = factor of standard (N/20) $K_2Cr_2O_7$ solution

$$= \frac{\text{wt. of } K_2Cr_2O_7 \text{ in 250 ml solution (w)}}{0.6129}$$

$$\text{Thus, total Mn in 250 ml} = 0.2282 \times \frac{w (V_1x - V_2)}{V} \text{ g.}$$

(b) Bromate oxidation method :

Let, V ml of sample Mn solution is oxidised to MnO_2 .

If 25 ml (N/20) Mohr solution

$$\equiv V_1 \text{ ml of f.(N/20) } K_2Cr_2O_7$$

and $(25 \times x)$ ml (N/20) Mohr solution

$$\equiv V_2 \text{ ml of f. (N/20) } K_2Cr_2O_7 + MnO_2 \text{ obtained from } V \text{ ml of sample Mn solution}$$

$\therefore MnO_2$ obtained from V ml of sample solution

$$\equiv (V_1x - V_2) \text{ ml of f. (N/20) } K_2Cr_2O_7$$

$$\therefore \frac{Cr_2O_7^{2-}}{6} \equiv Fe \equiv \frac{MnO_2}{2} \equiv \frac{Mn}{2} \equiv \frac{54.94}{2} \text{ g. of Mn}$$

$$\therefore 1000 \text{ ml of (N) } K_2Cr_2O_7 \equiv 27.47 \text{ g. of Mn.}$$

$$(V_1x - V_2) \text{ ml of f.(N/20) } K_2Cr_2O_7 \equiv \frac{27.47 \times (V_1x - V_2) \times f}{1000 \times 20} \text{ g. of Mn}$$

\therefore Total Mn in 250 ml stock solution

$$= \frac{27.47 \times (V_1x - V_2) \times f \times 250}{1000 \times 20 \times V} \text{ g.}$$

$$= 0.3434 \times f \times \left(\frac{V_1x - V_2}{V} \right) \text{ g.}$$

where, f = factor of (N/20) $K_2Cr_2O_7$ solution

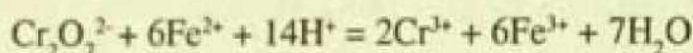
$$= \frac{\text{wt. of } K_2Cr_2O_7 \text{ in 250 ml solution (w)}}{0.6129}$$

$$\therefore \text{Total Mn in 250 ml} = 0.56 \times \frac{w (V_1x - V_2)}{V} \text{ g.}$$

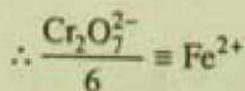
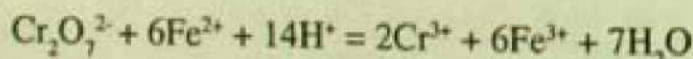
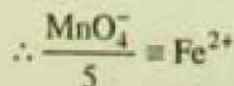
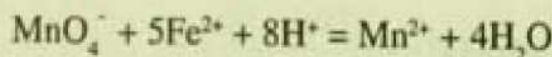
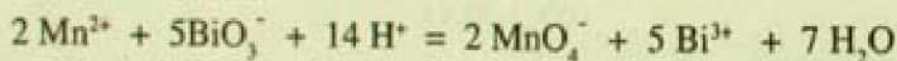
Experiment No. 12 : Estimation of Fe_2O_3 and MnO in Basic Slag

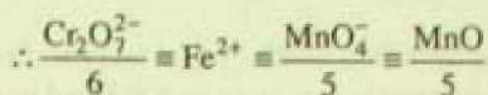
Principle :

Basic slag contains mainly Fe_2O_3 , CaO , MgO , MnO , P_2O_5 , SiO_2 and small amounts of Al_2O_3 , S , etc. A weighed quantity of finely powdered basic slag is brought into solution by digesting with 1:1 HCl . Fe^{3+} present in the solution is reduced to Fe^{2+} either by treating with Al -foil or with SnCl_2 or even by Jones reductor. Fe^{2+} is then titrated with standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution in the presence of NH_4HF_2 or syrupy H_3PO_4 using bariumdiphenylamine sulphate (BDS) indicator.



Mn^{2+} is oxidised to MnO_4^- with sodium bismuthate (NaBiO_3) in 2-3 (N) H_2SO_4 medium. The excess bismuthate is then filtered off through a sintered-glass or an asbestos-pulp bed. Resulting MnO_4^- is estimated in the presence of Fe^{2+} by adding a measured excess of standard Mohr's salt solution and then back titrating of the excess Mohr with standard $\text{Cr}_2\text{O}_7^{2-}$ solution using BDS indicator in presence of H_3PO_4 or NH_4HF_2 .





$$\equiv \frac{70.9394}{5} \text{ g. of MnO} \equiv 14.1874 \text{ g. of MnO}$$

$$\therefore 1000 \text{ ml of (N) K}_2\text{Cr}_2\text{O}_7 \text{ solution} \equiv 14.1874 \text{ g. of MnO}$$

For estimation of Mn the experimental solution should be freed from chloride by boiling with conc. H_2SO_4 , otherwise chloride will consume oxidant e.g. bismuthate, permanganate etc.

Chemicals and Apparatus required

- HCl (A.R.)
- H_2SO_4 (A.R.)
- Al – foil (A.R.)
- Syrupy H_3PO_4 / NH_4HF_2
- Barium diphenyleminesulphonate (BDS) indicator solution
- Standard (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution : To be prepared by accurate weighing.
- ~ (N/20) Mohr's salt solution.
- Asbestos pulp filter / sintered glass crucible.
- Suction filtering system.

Procedure :

1. Dissolution of Basic Slag :

Attack ~1.0 g of finely powdered basic slag with 30 ml of 6(N) HCl in a 500 ml conical flask, cover with a funnel and heat gently on asbestos board till dissolution. Evaporate almost to dryness over a low flame. Cool and add 10 ml of 6(N) HCl and evaporate as before. Repeat the process twice with two further 10 ml portions of the same acid. Finally fume with 10 ml of conc. H_2SO_4 , cool, dilute carefully with water and boil to dissolve the sulphate salts. Cool to room temperature and filter through Whatman No. 1 filter paper into a 250 ml volumetric flask, wash with very dilute H_2SO_4 , make up the volume and mix uniformly. The acidity of the resulting solution will be ~ 1.4 (N) in H_2SO_4 .

2. Estimation of Fe_2O_3 :

Pipette out 50 ml of the prepared solution in to a 500 ml conical flask and acidify with 25 ml of conc. HCl. Heat just to boiling and reduce Fe^{3+} ion with Al-foil. Cool the solution under tap water to room temperature. Dilute to 150 ml with distilled water to adjust the acidity $\sim 2-3$ (N). Add 2-3 g. of NH_4HF_2 (or, 5 ml syrupy H_3PO_4) and 4-5 drops of BDS indicator. Titrate with the standard (N/20) $K_2Cr_2O_7$ solution to violet end point.

3. Estimation of MnO :

Pipette out 50 ml of the stock solution in to a 250 ml beaker, add 20 ml distilled water and 4-5 ml of conc. H_2SO_4 to adjust the acidity to ~ 3 (N) and allow cool to room temperature. Oxidise Mn^{2+} to MnO_4^- with 0.5 g. of sodium bismuthate. Filter off the excess bismuthate through a sintered-glass crucible or through an asbestos pulp bed fitted with a suction pump. Wash with 2(N) H_2SO_4 till the washings are colourless.

To the combined filtrate and washings, add a measured excess (25/50/75, say $(25 \times x)$ ml) of standard ($\sim N/20$) Mohr's salt solution to discharge the permanganate colour. Dilute to 150 ml with 2(N) H_2SO_4 , add 2 g. of NH_4HF_2 (or, 5 ml of syrupy H_3PO_4) and 4-5 drops of BDS indicator. Titrate with the standard (N/20) $K_2Cr_2O_7$ solution to a violet end point. Calculate the amount of MnO from the difference in the titre values.

Calculation

Let, the volume of the MnO sample solution oxidised to $MnO_4^- = V$ ml

Let, 25 ml (N/20) Mohr's solution $\equiv V_1$ ml of f.(N/20) $K_2Cr_2O_7$

and $(25 \times x)$ ml (N/20) Mohrs solution

$\equiv V_2$ ml of f. (N/20) $K_2Cr_2O_7 + MnO_4^-$ obtained from V ml of sample solution

$\therefore MnO_4^-$ obtained from V ml of sample solution

$$\equiv (V_1 x - V_2) \text{ ml of f. (N/20) } K_2Cr_2O_7$$

$$\equiv \frac{14.1874 \times (V_1 x - V_2) \times f}{1000 \times 20} \text{ g. of MnO}$$

$$(\because 1000 \text{ ml of (N) } K_2Cr_2O_7 \equiv 14.1894 \text{ g. of MnO}).$$

∴ Total MnO dissolved in 250 ml of sample solution

$$\equiv \frac{14.1874 \times (V_1 x - V_2) \times f \times 250}{1000 \times 20 \times V} \text{ g.}$$

$$= 0.1773 \times f \times \left(\frac{V_1 x - V_2}{V} \right) \text{ g.}$$

where, f = factor of standard (N/20) $K_2Cr_2O_7$ solution.

$$= \frac{\text{wt. of } K_2Cr_2O_7 \text{ in 250 solution (w)}}{0.6129}$$

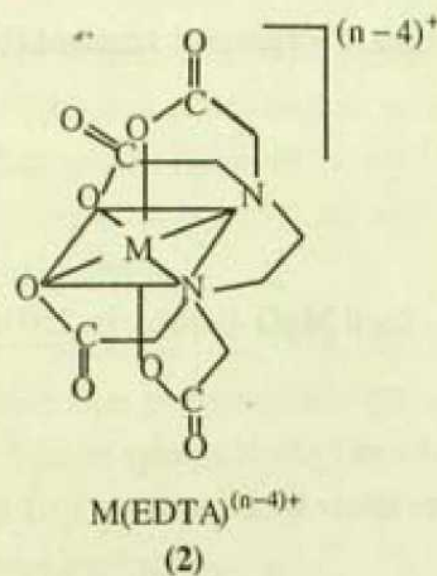
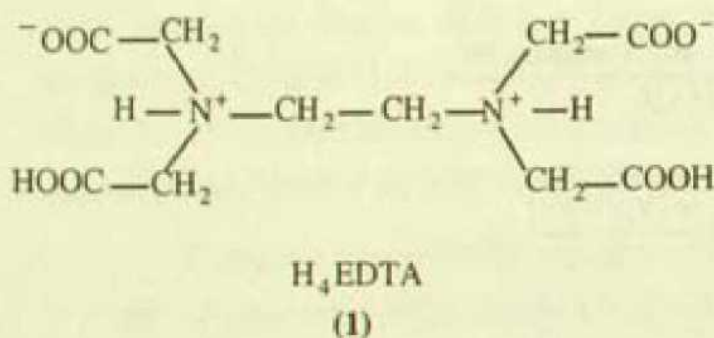
$$\therefore \text{Total MnO dissolve in 250 ml} = 0.2893 \times \frac{w (V_1 x - V_2)}{V} \text{ g.}$$

Chapter – 6

Titrimetric Estimations Based on Complexometric EDTA Titrations

General Principle :

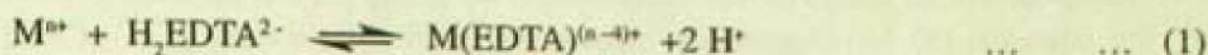
Ethylenediaminetetraacetic acid (EDTA) is a hexadentate ligand (1) and forms 1:1 complexes (2) of appreciably high stability constant (K) with most metal ions.



When such complex formation reactions are rapid and reversible, the metal ions may be quantitatively estimated by titrating known volume of their solutions with standard solution of EDTA (*direct titration*) or by titrating a known volume of standard solution of EDTA with the solutions of metal ions (*back titration*).

EDTA is commercially available in the form of its water soluble disodium salt, $\text{Na}_2\text{H}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ (F.W. = 372.24, also called EDTA) which, however, can not be used as a primary standard, as it may absorb some moisture and so it is to be standardised. Zinc acetate dihydrate, $\text{Zn}(\text{OOCCH}_3)_2 \cdot 2\text{H}_2\text{O}$ (F.W. = 219.38) is commonly used as the primary standard for standardisation of EDTA solution. Due to hydrolysis of acetate ion ($\text{pK}_{\text{CH}_3\text{COOH}}^{\text{H}} = 4.75$) aqueous solution of zinc acetate is alkaline and zinc hydroxide (solubility product: $K_{\text{sp}} \sim 10^{-15}$) is precipitated. To obtain a clear solution of zinc acetate, it is dissolved in 1-2% NH_4Cl solution, which acts as a buffer and is sufficiently acidic ($\text{pK}_{\text{NH}_4^+}^{\text{H}} = 9.2$) to prevent the precipitation of zinc hydroxide.

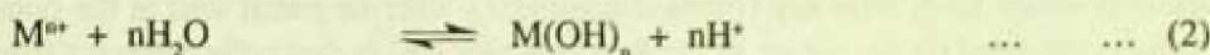
$\text{H}_2\text{EDTA}^{2-}$ reacts with metal ions liberating two moles of H^+ per mole of the metal ions (M^{n+} , $n=1,2,3,\dots$) :



$$\therefore [\text{M}^{n+}] \equiv [\text{EDTA}] \equiv 2 \text{H}^+$$

i.e., 1000 ml of (M) $\text{M}^{n+} \equiv$ 1000 ml of (M) EDTA solution \equiv 2000 ml of (M) H^+

Apparent stability of $\text{M}(\text{EDTA})$ complexes (charges omitted for simplicity) thus depends upon pH of the solution; it increases or decreases as pH increases or decreases. At lower pH, part of the EDTA may exist as its protonated forms : HEDTA^{3-} ($\text{pK}_1^{\text{H}} = 10.3$), $\text{H}_2\text{EDTA}^{2-}$ ($\text{pK}_2^{\text{H}} = 6.3$), H_3EDTA^- ($\text{pK}_3^{\text{H}} = 2.7$) and H_4EDTA ($\text{pK}_4^{\text{H}} = 2.0$), whereas, at higher pH, the metal ions and also the $\text{M}(\text{EDTA})$ complexes may undergo hydrolysis to precipitate metal hydroxides $\text{M}(\text{OH})_n$:



For each metal ion there is an optimum pH at which the formation of the $\text{M}(\text{EDTA})$ complex is maximum, i.e., equilibrium (1) is shifted to right and equilibria (2) and (3) are shifted to the left. To maintain the optimum pH value, EDTA titrations are always carried out in buffered solutions. There is also a chance of complex formation of the metal ions with the anions of the buffer solutions, as a result, stability of $\text{M}(\text{EDTA})$ complexes may be lowered. The dependence of stability of $\text{M}(\text{EDTA})$ complexes on protonation of EDTA species, metal ion hydrolysis and complex formation of metal ions with ligands other than EDTA may be expressed in terms of their apparent (conditional) stability constant (K') according to

$$\log K' = \log K - \log \alpha - \log \beta \quad \dots \quad (4)$$

where, $K = [\text{M}(\text{EDTA})] / ([\text{M}][\text{EDTA}])$

$$K' = [\text{M}(\text{EDTA})] / ([\text{conc. of M not bound to EDTA}] \times [\text{conc. of EDTA not bound to M}])$$

α = ratio of the sum of the concentrations of EDTA species not bound to M to the equilibrium concentrations of fully deprotonated free EDTA.

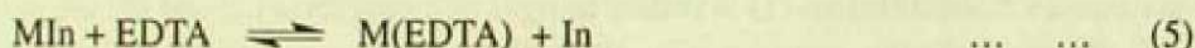
β = ratio of the sum of the concentrations of M species not bound to EDTA to the equilibrium concentrations of free M.

The factor, α , of EDTA at any pH may be calculated from the protonation constants of EDTA^{4-} and the factor, β , at any pH may be calculated from the hydrolysis constants of

the metal ion and the stability constants of its complexes with the anion of the buffer solution. Stability constants (K) of M-EDTA complexes may be obtained from literature. Thus K , α and β being known, K' values of M-EDTA complexes at any pH can be readily calculated using the equation (4). For quantitative estimation, the minimum value of K' of M-EDTA complexes should be as high as 10^8 and EDTA titration of the metal ions may be carried out at the corresponding pH values. Optimum pH values for EDTA titrations of some common metal ions are given below :

M^{n+}	Fe^{3+}	Al^{3+}	Cu^{2+}	Zn^{2+}	Mg^{2+}	Ca^{2+}
Optimum pH	2	5-8	5-10	9-10	10-12	10-12

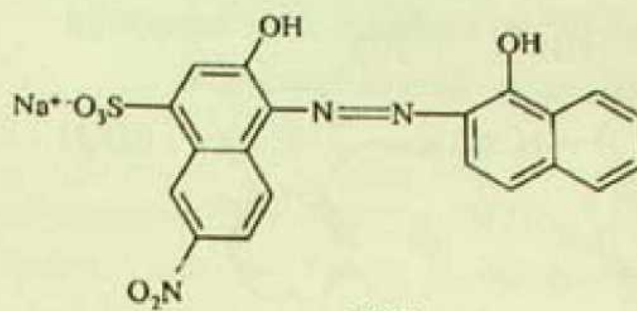
When a metal ion is titrated with EDTA, initially the pM value ($-\log[M]$) increases gradually, then there occurs an abrupt change of pM value at the equivalence point, after which it again increases gradually with further addition of EDTA. End point of complexometric EDTA titrations may be determined using suitable indicators (*metal indicators*) which form intensely coloured complexes with the metal ions at the optimum pH values, provided (i) the colour of the free indicator (In) is distinctly different from the colour of the metal-indicator complex (M-In), (ii) the reaction between the indicator and the metal ion is rapid and reversible and (iii) the apparent stability constant of M-In complex is lower than that of the M-EDTA complex, so that the displacement reaction (5)



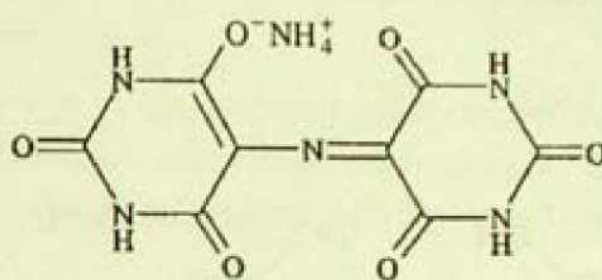
is quantitatively right shifted in the neighborhood of the equivalence point.

Some common metal indicators used in complexometric EDTA titrations are listed below :

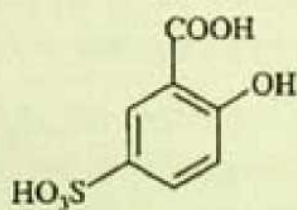
Indicator (In)	Colour		Metal (pH range)
	In	M-In	
1. Eriochrome Black – T (EBT)	Blue	Wine red	Ca, Mg, Zn (7–11)
2. Murexide	Blue-violet	Red-yellow	Ca(12), Cu, Ni, Co(10–11)
3. 1-Pyridyl-(2-azonaphthol)[PAN]	Yellow	Red-violet	Cu, Zn (4–6)
4. Patton-Reeders indicator	Pure blue	Red	Ca (12 – 14)
5. Calcon	Pure blue	Pink	Ca (12)
6. Xylenol orange	Lemon yellow	Red	Bi (1- 2), Zn, Pb (5)
7. Variamine Blue	Colourless (Reduced)	Blue (Oxidised)	Fe^{III} (2 - 3)
8. Sulfosalicylic acid	Colourless	Violet	Fe^{III} (2 - 3)
9. Ammonium thiocyanate	Colourless	Red	Fe^{III} (2 - 3)
10. Benzidine- $K_3Fe(CN)_6$ - $K_4Fe(CN)_6$	Colourless	Blue	Zn (6 - 10)



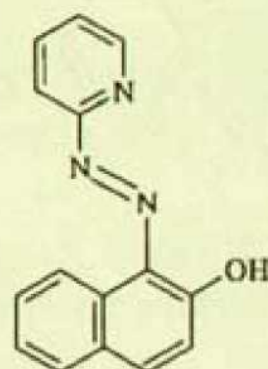
EBT



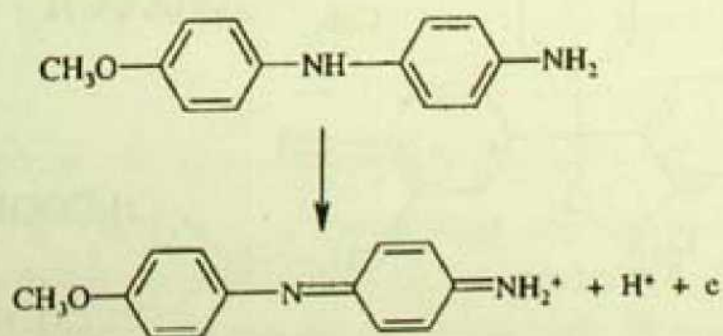
Murexide



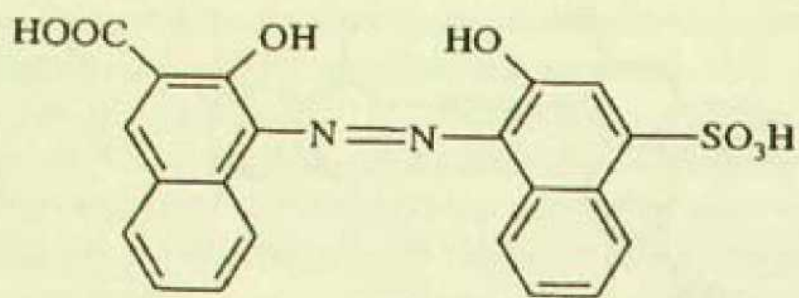
5-Sulfosalicylic acid



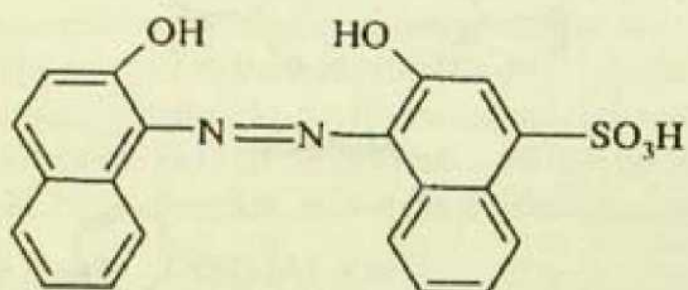
PAN [1-(2-pyridylazo)-2-naphthol]



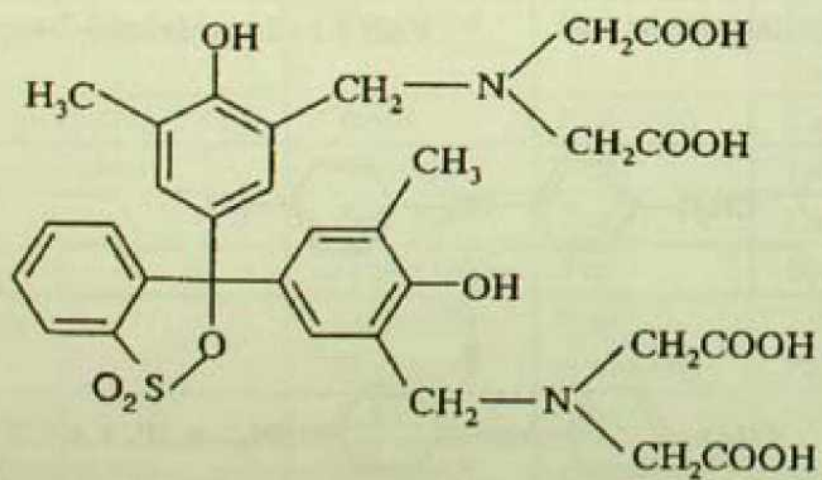
Variamine Blue



Patton - Reeder's indicator



Calcon



Xylenol orange

Experiment No -1 : Preparation of Standard (M/50) Zinc acetate solution and Standardisation of ~-(M/50) EDTA solution

Principle :

Zinc acetate dihydrate, $\text{Zn}(\text{OOCCH}_3)_2 \cdot 2\text{H}_2\text{O}$, is a salt of weak base and weak acid. In aqueous solution it undergoes hydrolysis, precipitating $\text{Zn}(\text{OH})_2$. To prevent its hydrolysis, zinc acetate is dissolved in ammonium chloride solution, which acts as a buffer (pH ~ 4-5). Since it is a primary standard substance, standard solution of zinc acetate can be prepared by dissolving directly weighed quantity of the salt in ammonium chloride solution and then diluting to definite volume.

EDTA solution may be standardized against standard zinc acetate solution in the presence of ammonium chloride-ammonia buffer solution (pH 10) using Eriochrome Black T (EBT) as indicator. The end point is indicated by change of colour from wine red to blue.

Chemicals required :

1. A.R. $\text{Zn}(\text{OOCCH}_3)_2 \cdot 2\text{H}_2\text{O}$ (F.W. = 219.38)
2. ~M/50 solution of $\text{Na}_2\text{H}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ (F. W. = 372.24) : 250 ml of (M/50) solution requires 1.8618 g. of $\text{Na}_2\text{H}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$. Dissolve about 2 g. of A.R. $\text{Na}_2\text{H}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ in deionised or distilled water and dilute to 250 ml.
3. NH_4Cl - NH_3 buffer solution of pH 10 : Dissolve 17.5g. of A.R. NH_4Cl in 142ml of conc. NH_3 (sp.gr.0.88 - 0.90) and dilute to 250 ml with water. Use 5 ml of this buffer solution per titration of 50 ml of the test solution.
4. Eriochrome Black T (EBT) : 0.4% methanolic solution of the dyestuff, which is stable for a month. Alternatively, grind a mixture of 0.05 g dye stuff with 5.0 g of A. R. KNO_3 or KCl or NaCl in a glass mortar, mix thoroughly. Use 30-50 mg (i.e., a pinch) of this indicator mixture for each titration.

Procedure :

1. Preparation of 250 ml ~-(M/50) zinc acetate dihydrate solution :

Place 5 g. of A.R. NH_4Cl into a 250 ml volumetric flask and dissolve the salt in ~50 ml distilled water. Weigh out accurately ~1.1g. (w.g. say) of A.R. Zn-acetate dihydrate and transfer the same quantitatively into the volumetric flask. Shake to dissolve the salt. Make up the volume with deionised or distilled water and shake well to mix uniformly. Strength of zinc acetate = $(w/1.0969)$ (M/50).

2. Standardisation of EDTA solution :

Take an aliquot of 25 ml of the standard (M/50) zinc acetate solution in a 250 conical flask, add 5 ml of $\text{NH}_3 - \text{NH}_4\text{Cl}$ buffer solution ($\text{pH} = 10$) and a pinch of EBT indicator. Titrate the solution with ($\sim \text{M}/50$) EDTA solution till the colour changes from wine red to blue.

Calculation :

$$V(\text{zinc acetate}) \times S(\text{zinc acetate}) = V(\text{EDTA}) \times S(\text{EDTA})$$

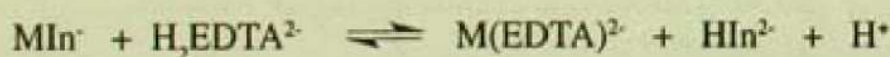
$$25 \times \frac{w}{1.0969} (\text{M}/50) = V(\text{EDTA}) \times S(\text{EDTA})$$

$$\therefore S(\text{EDTA}) = \left(\frac{25 \times w}{1.0969 \times V(\text{EDTA})} \right) (\text{M}/50)$$

Experiment-2 : Complexometric estimation of single metal ion : (i) Mg^{2+} & (ii) Ca^{2+}

Principle :

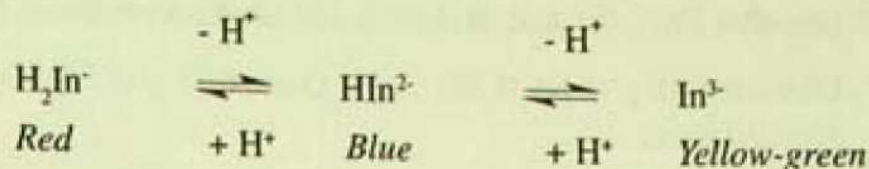
Both Ca^{2+} and Mg^{2+} ions form 1:1 complexes with EDTA as well as with the indicator Eriochrome Black T (EBT) at pH 10. Mg-EDTA complex is less stable than Ca-EDTA complex, but Mg-indicator complex (MgIn^-) is more stable than Ca-indicator complex (CaIn^-), while in both cases M-EDTA complexes ($\text{M} = \text{Mg}^{2+}, \text{Ca}^{2+}$) are more stable than the M-indicator complexes. During the titration, EDTA at first reacts with free metal ions to form M-EDTA complexes and then reacts with the wine-red coloured MIn^- complexes releasing free indicator.



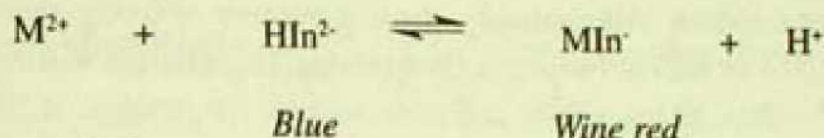
Wine red

Blue

At $\text{pH} < 5.5$, EBT (NaH_2In) solution is red due to H_2In^- ; between pH 7 and 11, it is blue due to HIn^{2-} . At $\text{pH} > 11.5$, it is yellowish-orange due to In^{3-} :



In the pH range 7-11, the addition of indicator EBT (blue) to the metal ion solution, changes the colour from blue to wine red :



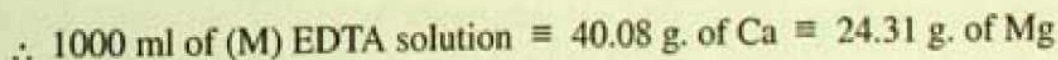
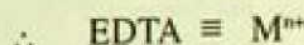
In the estimation of the metal ions by titrating with EDTA solution in the presence of EBT indicator, the colour of the solution changes from wine red to blue at the end point.

As Ca^{2+} ion forms a relatively more stable complex with EDTA but much less stable complex with EBT indicator, no sharp end point with EBT indicator is obtained with Ca^{2+} ion alone. To obtain sharp end point, a small amount of 0.1 (M) Na_2MgEDTA solution may be added to the Ca^{2+} solution before titration. As a result more stable Na_2CaEDTA will be formed in solution releasing equivalent amount of Mg^{2+} :



The released Mg^{2+} ions then react with EBT indicator to form the wine red coloured MgIn^- complex. On titration with EDTA in presence of $\text{NH}_4\text{Cl-NH}_3$ buffer (pH – 10) the colour of the solution changes from wine red to blue at the end point.

As EDTA forms 1:1 complex with metal ions :



Chemicals required :

1. Standard (M/50) Zn-acetate solution, $\text{Zn(OOCCH}_3)_2 \cdot 2\text{H}_2\text{O}$ (F.W. = 219.38) :
(c.f. Experiment No. 1)
2. (~M/50) solution of $\text{Na}_2\text{H}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ (F. W. = 372.24) (c.f. Experiment No. 1)
3. NH_3 - NH_4Cl buffer solution of pH 10 containing a small amount of Mg-EDTA complex :

- (a) Dissolve 17.5g. of A.R. NH_4Cl in 142ml of concentrated NH_3 (sp. gr. 0.88 - 0.90).
- (b) Dissolve 1.18 g. of $\text{Na}_2\text{H}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ and 0.78 g. of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in 50ml deionised/ distilled water.

Mix the solutions (a) and (b) and dilute to 250ml with deionised/distilled water. Use 5ml of this buffer solution for titration of 50 ml of the test solution.

- (4) Eriochrome Black T (EBT) : 0.4% methanolic solution of the dyestuff which is stable for a month. Alternatively, grind a mixture of 0.05g. dyestuff with 5.0g. of (A. R.) KNO_3 or KCl or NaCl in a glass mortar. This mixture will contain ~1% of the indicator. Use 30 - 50 mg. of the indicator mixture for titration of 50 ml of the test solution.
- (5) Unknown metal ion solutions:
 - (a) (~M/50) $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$: ~5 g/litre in 2(N) H_2SO_4
 - (b) (~M/50) CaCl_2 solution: Dissolve 2g. of CaCO_3 in minimum volume of 6(N)HCl and dilute to litre.

Procedure :

1. Standardisation of EDTA solution : (c.f. Experiment No. 1)

If w.g. of $\text{Zn}(\text{OOCCH}_3)_2 \cdot 2\text{H}_2\text{O}$ is present in 250 ml of the (M/50) solution, then strength of zinc-acetate solution is $= \frac{w}{1.0969}(\text{M}/50)$

If 25 ml of $\frac{w}{1.0969}(\text{M}/50)$ zinc acetate $\equiv V_1$ ml of EDTA,

$$\text{Then strength of EDTA} = \left(\frac{w \times 25}{1.0969 \times V_1} \right) (\text{M}/50)$$

2. Estimation of Mg^{2+} :

Transfer the supplied solution of the sample into a 100 ml volumetric flask and make up to the mark with distilled water.

Pipette out 25 ml of the diluted Mg^{2+} solution into a 250 ml conical flask, dilute with 25 ml of deionised or distilled water, add 5 ml of NH_4Cl - NH_3 buffer solution and a pinch (~50 mg) of Eriochrome black T indicator (or 3-4 drops of the indicator solution). Shake, when the colour of the solution turns wine red. Titrate the solution with standard

(~M/50) EDTA solution till the wine red colour turns pure blue. Titrate slowly near the end point.

Calculation :

Let 25 ml Mg^{2+} solution $\equiv V_2$ ml EDTA

\therefore 1000 ml of (M) EDTA \equiv 24.31 g. of Mg

$$\therefore V_2 \text{ ml of } \left(\frac{w \times 25}{1.0969 \times V_1} \right) (M/50) \text{ EDTA} \equiv \left(\frac{24.31 \times w \times 25 \times V_2}{1000 \times 1.0969 \times V_1 \times 50} \right) \text{ g. of Mg.}$$

\therefore Total Mg in 100 ml solution

$$= \left(\frac{24.31 \times w \times 25 \times V_2 \times 100}{1000 \times 1.0969 \times V_1 \times 50 \times 25} \right) \text{ g. of Mg}$$

$$= \left(\frac{24.31 \times 0.002}{1.0969} \right) \times \left(\frac{w \times V_2}{V_1} \right) \text{ g. of Mg}$$

$$= 0.044 \times \left(\frac{w \cdot V_2}{V_1} \right) \text{ g of Mg}$$

3. Estimation of Ca^{2+} :

Transfer the supplied solution of the sample quantitatively into a 100 ml volumetric flask, make up to the mark with distilled water and mix uniformly.

Pipette out 25 ml of the diluted Ca^{2+} solution in a 250 ml conical flask, dilute with 25 ml deionised/distilled water, add 5 ml of NH_4Cl-NH_3 buffer solution of pH 10 containing a little of Mg-EDTA complex and a pinch (~50 mg) of Eriochrome black T indicator (or 3-4 drops of the indicator solution). Shake, when the colour of the solution turns wine red. Titrate the solution with standard (~ M/50) EDTA solution till the wine red colour turns pure blue. Titrate slowly near the end point.

Calculation :

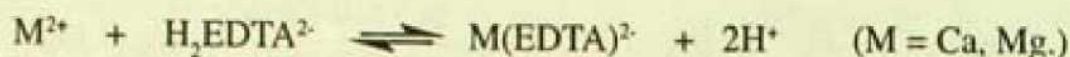
If 25 ml of Ca^{2+} solution $\equiv V_3$ ml of EDTA, then, following the same procedure as in Mg^{2+} one obtains :

$$\begin{aligned} \text{Total } Ca^{2+} \text{ in 100 ml solution} &= \left(\frac{40.08 \times 0.002}{1.0969} \times \frac{w V_3}{V_1} \right) \text{ g. of Ca} \\ &= 0.0731 \times \left(\frac{w \cdot V_3}{V_1} \right) \text{ g. of Ca} \end{aligned}$$

Experiment-3 : Complexometric Estimation of Ca^{2+} and Mg^{2+} in mixture

Principle :

Complexometric titration of $\text{Mg}^{2+} + \text{Ca}^{2+}$ mixture with EDTA in $\text{NH}_4\text{Cl}-\text{NH}_3$ buffer medium (pH 10) gives the sum of the total amount of Mg^{2+} and Ca^{2+} present in the mixture. EDTA titration of the mixture in strongly alkaline medium (pH 12), at which Mg^{2+} is precipitated as $\text{Mg}(\text{OH})_2$ but Ca^{2+} remains in solution, gives the amount of Ca^{2+} in the mixture.



1000 ml of (M) EDTA solution \equiv 40.08 g. of Ca \equiv 24.31 g. of Mg

Chemical required : Same as in experiments 1 and 2.

Additional reagents :

- (i) 10% NaOH solution
- (ii) Patton – Reeder's indicator mixture

Procedure :

1. Standardisation of EDTA solution : (cf. Experiment 1, Titre of EDTA = V_1 ml).
2. Transfer the supplied solution of the sample quantitatively into a 250 ml volumetric flask, make up to the mark with distilled water and mix uniformly.
3. Estimation of $(\text{Ca}^{2+} + \text{Mg}^{2+})$:

Pipette out 25 ml of the supplied mixture in a 250 ml conical flask. Add 1-2 drops methyl red indicator. The solution turns red. Neutralise with drops of (1:1) aqueous – NH_3 to a just yellow colour and then add 5 ml of $\text{NH}_4\text{Cl}-\text{NH}_3$ buffer solution (pH 10) and a pinch (~50 mg) of Eriochrome black T indicator (or 3-4 drops of the indicator solution), when the colour of the solution turns wine red. Titrate the solution with standard (~M/50) EDTA solution till the wine red colour turns pure blue. Titrate slowly near the end point. This titre value (V_2) gives total of $(\text{Ca}^{2+} + \text{Mg}^{2+})$.

4. Estimation of Ca^{2+} :

Pipette out 25 ml of the mixture solution in a 250 ml conical flask. Add 1-2 drops of methyl red indicator. The solution turns red. Neutralise with drops of 10% NaOH solution to a just yellow colour and then add 10 ml of the 10% NaOH solution, mix well and add a pinch (~50 mg) of Patton-Reeder's indicator mixture. Shake, when the colour of the solution turns wine red. Titrate the solution with standard ~M/50 EDTA solution till the wine red colour turns pure blue. This titre value (V_3) gives the amount of Ca^{2+} and the difference ($V_2 - V_3$) gives the amount of Mg^{2+} .

5. Calculate separately the amounts of Ca and Mg present in the supplied solution.

Calculation :

Strength of standard Zn acetate = $(w/1.0969)(M/50)$.

where, w = wt. of Zn $(CH_3COO)_2 \cdot 2H_2O$ in 250 ml solution.

Let, 25 ml of standard $Zn^{2+} \equiv V_1$ ml of EDTA

$$\therefore \text{Strength of EDTA} = \left(\frac{25 \times w}{1.0969 \times V_1} \right) (M/50)$$

\therefore 1000 ml of (M) EDTA \equiv 40.08 g. of Ca \equiv 24.31 g. of Mg.

$$Ca^{2+} \text{ in 25 ml of sample solution} = \left(\frac{40.08 \times V_3 \times 25 \times w}{1000 \times 1.0969 \times V_1 \times 50} \right) g.$$

\therefore Total Ca^{2+} in 250 ml of sample solution

$$= \left(\frac{40.08 \times V_3 \times 25 \times 250}{1000 \times 1.0969 \times 50 \times 25} \right) \times (w V_3/V_1) g$$

$$= 40.08 \times (4.558 \times 10^{-3}) (w V_3/V_1) g.$$

$$= 0.1827 \times (w V_3/V_1) g.$$

Similarly total Mg^{2+} in 250 of sample solution

$$= \left(\frac{24.31 \times 25 \times 250}{1000 \times 1.0969 \times 50 \times 25} \right) \times \left[\frac{w(V_2 - V_3)}{V_1} \right] g$$

$$= 24.31 \times (4.558 \times 10^{-3}) \times w(V_2 - V_3)/V_1 g.$$

$$= 0.1108 \times w(V_2 - V_3) / V_1 g.$$

Experiment No. – 4 : Complexometric Estimation of $CaCO_3$ and $MgCO_3$ in Dolomite

Principle :

Dolomite contains $CaCO_3$ and $MgCO_3$ as major components and SiO_2 and Fe_2O_3 as trace constituents. The ore is attacked with HCl, when $CaCO_3$, $MgCO_3$ and Fe_2O_3 pass into solution and SiO_2 remains insoluble. Ca^{2+} and Mg^{2+} in the solution may be estimated by titrating with EDTA- at pH 10 (NH_4Cl-NH_3 buffer) using EBT indicator. Ca alone may be estimated by EDTA titration at pH 12-14 (NaOH) using Patton-Reedrer's indicator or murexide indicator. For very accurate work Fe^{3+} alone may be estimated by EDTA titration at pH ~ 2-3 using NH_4SCN or sulfosalicylic acid as indicator.

Chemicals required :

1. Dolomite ore.
2. Conc. HCl (A.R).
3. Conc. HNO_3 (A.R).
4. Standard (M/50) zinc acetate solution.
5. ~ (M/50) EDTA solution.
6. $\text{NH}_4\text{Cl} - \text{NH}_3$ buffer solution.
7. 10% NaOH solution.
8. Eriochrome Black – T indicator.
9. Patton – Reeders indicator or Murexide indicator.
10. 5% NH_4SCN solution or 5% sulfosalicylic acid solution in water.

Procedure :

1. Dissolution of Dolomite :

Weigh out accurately ~1.0 g. of the finely powdered dolomite ore in a 250 ml beaker. Moisten it with water and add 40 ml 1:1 HCl. Heat the beaker gently over a low flame on an asbestos board till the dissolution is complete. Add 2 ml of conc. HNO_3 and 10 ml of 1:1 HCl, evaporate nearly to dryness. Repeat this operation twice using 10 ml of 1:1 HCl. Bake the solid mass for 5-10 minutes. Cool to room temperature. Add 5 ml of conc. HCl and 50 ml water and warm to obtain a clear solution. Transfer the solution quantitatively into a 250 ml volumetric flask by washing with distilled water. Make up the volume upto the mark and mix uniformly and allow the SiO_2 (if any) to settle down.

2. Standardisation of EDTA solution (cf. Experiment No. 3).
3. Estimation of $(\text{CaCO}_3 + \text{MgCO}_3)$ (cf. Experiment No. 3).
4. Estimation of CaCO_3 (cf. Experiment No. 3).
5. Estimation of Fe_2O_3 (cf. Experiment No. 5)

Calculation :

$$\text{Strength of Zn-acetate} = \left(\frac{w}{1.0969} \right) (\text{M/50})$$

where, w = wt. of zinc acetate dihydrate in 250 ml solution.

Let, 25 ml of $\left(\frac{w}{1.0969}\right) (M/50) \text{ Zn}^{2+} \equiv V_1 \text{ ml of EDTA.}$

$(\text{Ca}^{2+} + \text{Mg}^{2+})$ in 25 ml of sample solution $\equiv V_2 \text{ ml of EDTA}$

Ca^{2+} in 25 ml of sample solution $\equiv V_3 \text{ ml of EDTA.}$

$\therefore \text{Mg}^{2+}$ in 25 ml of sample solution $\equiv (V_2 - V_3) \text{ ml of EDTA.}$

$\therefore \text{Strength of EDTA} = [(25 \times w) / (1.0969 \times V_1)] (M/50)$

$\therefore \text{EDTA} \equiv \text{Ca} \equiv \text{CaCO}_3 \equiv \text{Mg} \equiv \text{MgCO}_3$

$\therefore 1000 \text{ ml of (M) EDTA}$

$\equiv 40.08 \text{ g. of Ca} \equiv 100.08 \text{ g. of CaCO}_3$

$\equiv 24.31 \text{ g. of Mg} \equiv 84.31 \text{ g. of MgCO}_3$

Following the procedure as described in experiment No. 3 one obtains :

Total Ca^{2+} in 250 ml of sample solution

$$= 40.08 \times (4.558 \times 10^{-3}) \times (wV_3 / V_1) \text{ g.}$$

$$= 0.1827 \times (w V_3 / V_1) \text{ g.}$$

Total CaCO_3 in 250 ml sample solution

$$= 100.08 \times (4.558 \times 10^{-3}) \times (wV_3 / V_1) \text{ g}$$

$$= 0.4562 \times (wV_3 / V_1) \text{ g}$$

Total Mg^{2+} in 250 ml of sample solution

$$= 24.31 \times (4.558 \times 10^{-3}) \times [w(V_2 - V_3) / V_1] \text{ g}$$

$$= 0.1108 \times [w(V_2 - V_3) / V_1] \text{ g}$$

Total MgCO_3 in 250 ml sample solution

$$= 84.31 \times (4.558 \times 10^{-3}) \times [w(V_2 - V_3) / V_1] \text{ g}$$

$$= 0.3843 \times [w(V_2 - V_3) / V_1] \text{ g}$$

Experiment No. - 5 : Complexometric Estimation of Fe^{3+}

Principle :

In acid medium (at pH ~ 2-3) Fe^{III} forms very a stable EDTA complex, Fe^{III} (EDTA). Total amount of Fe^{III} in a given solution may be estimated by titrating with standard EDTA solution using sulfosalicylic acid (or NH_4SCN) as indicator which forms intense violet (or red) coloured complexes with Fe^{III} . Since Fe^{III} forms 1:1 complex with EDTA,



\therefore 1000 ml of (M) EDTA \equiv Fe \equiv 55.847 g. of Fe

$$\equiv \frac{\text{Fe}_2\text{O}_3}{2} \equiv \frac{159.692}{2} \text{ g. of Fe}_2\text{O}_3 \equiv 79.846 \text{ g. of Fe}_2\text{O}_3$$

Chemicals required :

- (1) Standard (M/50) solution of zinc acetate dihydrate (F.W. 219.38)
- (2) (~ M/50) solution of $\text{Na}_2\text{H}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ (F.W. 372.24)
- (3) Sulfosalicylic acid indicator: 5 % aqueous solution, or, NH_4SCN : 5 % aqueous solution.
- (4) EBT indicator.
- (5) 1:1 aqueous NH_3
- (6) Chloroacetic acid buffer (pH 2.3) : Mix 50 ml of 1(M) chloroacetic acid solution with 25 ml of 1(M) NaOH solution.

Procedure :

1. Transfer the supplied solution of the sample quantitatively with a 100 ml volumetric flask, make upto the mark with 2(N) H_2SO_4 and mix uniformly.
2. Standardise the EDTA solution against standard (M/50) zinc acetate solution. (cf. Experiment No. 1).
3. Estimation of total Fe^{III}

Take an aliquot of 25 ml of Fe^{III} solution into a 250 ml conical flask, neutralise with (1:1) aqueous NH_3 till a slight permanent turbidity appears. Add 5 ml of chloroacetic acid buffer (pH = 2.3) to obtain a just clear solution. Add 1 ml of sulfosalicylic acid or (NH_4SCN) indicator and titrate with the standard ~ (M/50) EDTA solution till the colour changes from violet (or, red) to colourless at the end point.

4. Calculate the amounts of Fe (or Fe_2O_3) present in the total volume of the prepared solution.

Calculation :

Strength of Zn-acetate = $(w / 1.0969)$ (M/50)

If 25 ml of standard zinc acetate $\equiv V_1$ ml of EDTA

Fe^{3+} in 25 ml of sample solution $\equiv V_2$ ml of EDTA

Then, strength of EDTA = $[(25 \times w) / (1.0969 \times V_1)]$ (M/50).

Fe^{3+} in 25 ml sample solution

$$= \left(\frac{55.847 \times V_2 \times 25 \times w}{1000 \times 1.0969 \times V_1 \times 50} \right) \text{ g.}$$

Total Fe^{3+} in 100 ml sample solution

$$= \left(\frac{55.847 \times 25 \times 100}{1000 \times 1.0969 \times 25 \times 50} \right) \times (w V_2 / V_1) \text{ g.}$$

$$= 55.847 \times (1.823 \times 10^{-3}) \times (w V_2 / V_1) \text{ g} = 0.1018 \times (w V_2 / V_1) \text{ g}$$

\therefore Total Fe_2O_3 in 100 ml of sample solution

$$= 79.846 \times (1.823 \times 10^{-3}) \times (w V_2 / V_1) \text{ g} = 0.1456 \times (w V_2 / V_1) \text{ g.}$$

Experiment No. - 6 : Complexometric Estimation of Al^{3+}

Principle :

In presence of ammonium acetate-ammonia buffer (pH 7-8) Al^{III} forms very stable EDTA complex, $\text{Al}(\text{EDTA})^-$. Amount of Al^{III} in a given solution may be estimated by adding measured excess of standard EDTA solution and back titrating the excess EDTA with standard zinc acetate solution using EBT indicator at pH 9-10. Since Al^{3+} forms 1:1 complex with EDTA,



$$\therefore 1000 \text{ ml of (M) EDTA} \equiv 26.98 \text{ g. of Al}$$

$$\equiv 1000 \text{ ml of (M) } \text{Al}^{3+}$$

$$\equiv 1000 \text{ ml of (M) } \text{Zn}^{2+}$$

Chemicals required :

- (1) Standard (M/50) zinc acetate dihydrate (F.W. 219.38) solution (cf. Experiment No. 1)
- (2) (~M/50) $\text{Na}_2\text{H}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ (F.W. 372.24) solution (cf. Experiment No. 1)
- (3) EBT indicator (cf. Experiment No. 1)
- (4) Ammonium acetate solid crystals.
- (5) $\text{NH}_4\text{Cl}-\text{NH}_3$ buffer pH 10 (cf. Experiment No. 1)

Procedure :

1. Transfer the supplied solution of the sample quantitatively into a 100 ml volumetric flask, make up to mark with 2(N) HCl and mix uniformly.

2. Standardisation of EDTA solution.

Take an aliquot of 25 ml of the (~ M/50) EDTA solution, dilute with 20 ml of water, add 5 ml of $\text{NH}_4\text{Cl-NH}_3$ buffer solution (pH 10) and a pinch of EBT indicator powder. The solution turns deep blue. Titrate with standard (M/50) Zn-acetate solution till the blue colour changes to wine red (titre = V_1 ml).

3. Estimation of Al^{3+} .

Pipette out an aliquot of 10 ml, or, 25 ml (say, V ml) of the Al^{3+} solution in a 250 ml conical flask and add a measured excess (50 ml, say $25 \times x$ ml) of standard (~M/50) EDTA solution. Add 2-3 drops of methyl red indicator. Neutralise with 1:1 aqueous NH_3 solution to just yellow colour, then add 2-3 g of ammonium acetate and a pinch of EBT indicator and a few drops of 1:1 aqueous NH_3 till the solution assumes a blue colour. If the solution is red, add another 25 ml of standard (M/50) EDTA and a few more drops of (1:1) aqueous- NH_3 to get a blue solution. Back titrate the excess EDTA with the standard (M/50) Zn-acetate solution till the colour of the solution changes from blue to wine red. (titre = V_2 ml)

4. Calculate the amount of Al present in the supplied solution.

Calculation :

Strength of Zn-acetate solution

$$= \frac{\text{wt. of zincacetate dihydrate in 250 ml}}{1.0969} \text{ (M/50)}$$

$$= \frac{w}{1.0969} \text{ (M/50)}$$

$$\therefore 25 \text{ ml of EDTA} \equiv V_1 \text{ ml of } (w/1.0969) \text{ (M/50) } \text{Zn}^{2+}$$

$$\therefore (25 \times x) \text{ ml of EDTA} \equiv V_1 \times x \text{ ml of } (w/1.0969) \text{ (M/50) } \text{Zn}^{2+}$$

$$(25 \times x) \text{ ml of EDTA} \equiv V_2 \text{ ml of } (w/1.0969) \text{ (M/50) } \text{Zn}^{2+} + V \text{ ml of sample } \text{Al}^{3+} \text{ solution}$$

$$\therefore V \text{ ml of sample } \text{Al}^{3+} \text{ solution}$$

$$\equiv (V_1 \times x - V_2) \text{ ml of } (w/1.0969) \text{ (M/50) } \text{Zn}^{2+}$$

$$\equiv \left[\frac{(V_1 x - V_2) \times w}{1.0969 \times 50} \right] \text{ ml of (M) } \text{Zn}^{2+}$$

$$\equiv \left[\frac{w \times (V_1 x - V_2)}{1.0969 \times 50} \right] \text{ ml of (M) } \text{Al}^{3+}$$

$\therefore 1000 \text{ ml of (M) Al}^{3+} \equiv 26.98 \text{ g of Al}$

\therefore Amount of Al in V ml of the sample solution

$$= \frac{26.98}{1000} \times \left[\frac{w(V_1x - V_2)}{1.0969 \times 50} \right] \text{ g.}$$

If the total volume of the sample Al solution is 100 ml, then

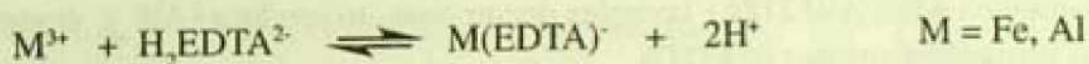
$$\begin{aligned} \text{Total Al} &= \left(\frac{26.98 \times 100}{1000 \times 1.0969 \times 50} \right) \times \frac{w(V_1x - V_2)}{V} \text{ g.} \\ &= 26.98 \times (1.823 \times 10^{-3}) \times [w(V_1x - V_2)/V] \text{ g.} \\ &= 0.0492 \times [w(V_1x - V_2)/V] \text{ g.} \end{aligned}$$

Experiment No. -7 : Complexometric Estimation of Fe^{3+} and Al^{3+} in mixture

Principle :

In presence of acetate buffer both Fe^{III} and Al^{III} form very stable EDTA complexes. $\text{Fe}(\text{EDTA})^-$ complex is more stable than $[\text{FeF}_6]^{3-}$ complex, but $\text{Al}(\text{EDTA})^-$ is less stable than $[\text{AlF}_6]^{3-}$. Total amount of (Fe + Al) may be estimated by treating the mixture with a measured excess of standard EDTA solution and then back titrating the excess EDTA with standard zinc acetate solution using xylenol orange or PAN or EBT as indicator in appropriate buffer medium. On boiling the above titrated solution with an excess of NH_4F , the $\text{Al}(\text{EDTA})^-$ complex decomposes and $[\text{AlF}_6]^{3-}$ is produced, liberating an equivalent amount of EDTA. The liberated EDTA is then titrated with the same standard zinc acetate solution using the same indicator. This gives the amount of Al^{III} in the mixture and the difference gives the amount of Fe^{III} .

As both Fe^{III} and Al^{III} form 1:1 complexes with EDTA,



$$\therefore \text{EDTA} \equiv \text{Fe} \equiv \text{Al}$$

$$\begin{aligned} \therefore 1000 \text{ ml of (M) EDTA} &\equiv 55.847 \text{ g. of Fe} \equiv 26.98 \text{ g. of Al} \\ &\equiv 1000 \text{ ml of (M) Zn}^{2+} \end{aligned}$$

Chemicals required :

- (1) Standard (M/50) of zinc acetate dihydrate (F.W. 219.38) solution
- (2) (~ M/50) of $\text{Na}_2\text{H}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ (F.W. 372.24) solution.

- (3) (i) Xylenol orange indicator : 0.5 % solution in ethanol.
(ii) PAN indicator solution : 0.1% solution in ethanol or methanol.
- (4) Acetate buffer : Mix equal volume of each of 0.5 M sodium acetate and 0.5 M acetic acid (pH = 4 ~ 5).
- (5) (~M/50) ($\text{Fe}^{3+} + \text{Al}^{3+}$) mixture : Dissolve 12 g. of each of A.R. potash alum ($\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$) and A. R. ammoniumferric alum ($(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$) in 2(N) H_2SO_4 and dilute to 1 litre with the same acid.

Procedure : (a) Using Xylenol orange indicator

- (i) Standardisation of EDTA solution :

Take an aliquot of 25 ml of the (~ M/50) EDTA solution in a 250 ml conical flask, dilute with 20 ml of water and add 5 ml of the acetate buffer solution and 2-3 drops of xylenol orange indicator. Titrate with standard (M/50) zinc acetate solution till the colour of the solution changes from yellow to red. (titre : V_1 ml).

- (ii) Estimation of total ($\text{Fe}^{III} + \text{Al}^{III}$) :

Pipette out 25ml of the ($\text{Fe}^{3+} + \text{Al}^{3+}$) mixture in a 250 ml conical flask, add a measured excess (50 ml say $(25 \times x)$ ml) of standard (~M/50) EDTA solution. Add 2-3 drops of methyl red indicator. Neutralise with (1:1) aqueous NH_3 solution to just yellow colour. To the resulting solution add 2-3 drops of xylenol orange indicator and 10 ml of acetate buffer (pH 4 ~ 5). The solution should assume a lemon yellow colour. If the solution is not yellow, add another 25 ml of standard (M/50) EDTA and a few drops of (1:1) aqueous NH_3 to get the yellow colour. Back titrate the excess EDTA with the standard (M/50) Zn-acetate solution till the colour changes from yellow to red. (titre = V_2 ml)

- (iii) Estimation of Al^{3+} :

To the above back titrated solution add 1.5-2 g. of NH_4F and boil for about 5 minutes when $\text{Al}(\text{EDTA})^-$ complex decomposes to produce $[\text{AlF}_6]^{3-}$ complex and liberates an equivalent amount of EDTA.



The colour of the solution changes again to yellow. Allow the solution to cool to room temperature and add another 5 ml of acetate buffer to the resulting yellow solution and 2-3 drops of xylenol orange indicator, (if necessary), to restore the same yellow colour. Titrate the liberated EDTA with the same standard (M/50) Zn-acetate solution till the colour changes from yellow to red. (titre = V_3 ml).

- (iv) Calculate separately the amounts of Fe and Al present in the supplied solution.

Procedure : (b) Using PAN indicator :

- (i) Standardise the EDTA solution by titrating with standard (M/50) Zn-acetate in acetic acid-acetate buffer medium (pH ~ 5) using PAN indicator, colour change at the end point will be from yellow to red. (titre = V_1 ml).
- (ii) Take an aliquot of 25 ml of the ($\text{Fe}^{3+} + \text{Al}^{3+}$) mixture in to a 250 ml conical flask and neutralise with 1:1 aqueous NH_3 till a slight permanent turbidity appears. Add drops of very dil. HCl to have a clear solution. Now add a measured excess (50 ml, say $(25 \times x)$ ml) of standard EDTA solution to complex both the metal ions. Add 10 ml acetate buffer and heat to boiling. Add 4-5 drops PAN indicator. Colour of the solution should be yellow if EDTA is in excess. Otherwise, add another 25 ml of the EDTA solution and a few drops of (1:1) aqueous - NH_3 to get the yellow colour. Back titrate the excess EDTA with standard (M/50) zinc acetate solution till the color of the solution changes from yellow to red. This titre value (V_2) corresponds to the sum of ($\text{Al}^{3+} + \text{Fe}^{3+}$).
- (iii) Add 1.5 – 2 g. of NH_4F to this back titrated solution and boil for another 5 minutes. The colour of the solution changes to yellow. Titrate the EDTA liberated from the $\text{Al}(\text{EDTA})^-$ complex in the hot condition with the same standard (M/50) zinc acetate solution till the colour of the solution changes from yellow to red. This titre value (V_3) corresponds to Al^{3+} . Calculate the amount of Fe^{3+} from the difference.

Notes :

- (1) Add 2-3 drops of the indicator if the solution is not sufficiently yellow after boiling with NH_4F .
- (2) This estimation can also be carried out using EBT as the indicator in ammonium-acetate-ammonia buffer (pH 7~8) following similar procedure.(cf. Experiment No. 6).

Calculation :

If 25 ml of EDTA solution $\equiv V_1$ ml of f.(M/50) zinc acetate solution

$(25 \times x)$ ml of EDTA $\equiv V_1 \times x$ ml of f. (M/50) zinc acetate.

If $(25 \times x)$ ml EDTA $\equiv 25$ ml ($\text{Al}^{3+} + \text{Fe}^{3+}$) mixture + V_2 ml of f.(M/50) zinc acetate

$\therefore 25$ ml ($\text{Al}^{3+} + \text{Fe}^{3+}$) mixture $\equiv (V_1 \times x - V_2)$ ml of f.(M/50) zinc acetate.

If Al^{3+} in 25 ml mixture $\equiv V_3$ ml of f.(M/50) zinc acetate,

then, Fe^{3+} in 25 ml mixture $\equiv (V_1 \times x - V_2 - V_3)$ ml of f.(M/50) zinc acetate.

where, f = factor of (M/50) zinc acetate solution = $(w/1.0969)$,

where, w = wt. of $\text{Zn}(\text{OOCCH}_3)_2 \cdot 2\text{H}_2\text{O}$ in 250 ml solution.

$\therefore \text{Al} \equiv \text{Al(EDTA)} \equiv \text{EDTA} \equiv \text{Zn(EDTA)} \equiv \text{Zn acetate}$

$\therefore V_3 \text{ ml of f.(M/50) zinc acetate} = \frac{26.98 \times V_3 \times f}{1000 \times 50} \text{ g. of Al}$

($\therefore 1000 \text{ ml of (M) Zinc acetate} \equiv 26.98 \text{ g of Al}$).

Total Al in 250 ml solution

$$\begin{aligned} &= \frac{26.98 \times V_3 \times f \times 250}{1000 \times 50 \times 25} \text{ g.} \\ &= 26.98 \times (2 \times 10^{-4}) \times (fV_3) \text{ g.} \\ &= (5.396 \times 10^{-3}) \times (fV_3) \text{ g.} \end{aligned}$$

$\therefore \text{Fe} \equiv \text{Fe (EDTA)} \equiv \text{EDTA} \equiv \text{Zn (EDTA)} \equiv \text{Zn acetate}$

$\therefore 1000 \text{ ml of (M) Zn-acetate} \equiv 55.847 \text{ g. of Fe}$

$\therefore (V_1 x - V_2 - V_3) \text{ ml of f.(M/50) zinc acetate}$

$$= \frac{55.847 \times (V_1 x - V_2 - V_3) \times f}{1000 \times 50} \text{ g. of Fe}$$

\therefore Total Fe in 250 ml solution

$$\begin{aligned} &= \frac{55.847 \times (V_1 x - V_2 - V_3) \times f \times 250}{1000 \times 50 \times 25} \text{ g. of Fe} \\ &= 55.847 \times (2 \times 10^{-4}) \times f \times [V_1 x - V_2 - V_3] \text{ g.} \\ &= 0.01117 \times f \times [V_1 x - V_2 - V_3] \text{ g.} \end{aligned}$$

Experiment No. -8: Complexometric Estimation of Fe^{3+} and Ca^{2+} in mixture

Principle :

Stability constant of $\text{Fe}^{III} (\text{EDTA})^-$ complex ($\log K = 25.1$) is much higher than that of $\text{Ca}^{II} (\text{EDTA})^{2-}$ complex ($\log K = 10.7$). That is why the optimum pH for EDTA titration for Fe^{3+} (pH=2-3) is much lower than that for Ca^{2+} (pH=10-12). Direct titration of the mixture with EDTA at pH=2-3 gives to Fe^{3+} only. If a measured excess of standard EDTA is added to Fe^{3+} and Ca^{2+} mixture and pH of the solution is adjusted to pH=10 (NH_3 - NH_4Cl buffer), both Fe^{3+} and Ca^{2+} are converted to their EDTA complexes. Back titration of the excess EDTA with a standard (M/50) Zn^{2+} solution gives the total of Fe^{3+} and Ca^{2+} . The amount of Ca^{2+} may then be obtained from the difference.

As both Fe^{3+} and Ca^{2+} form 1:1 complexes with EDTA.



\therefore 1000 ml of (M) EDTA solution \equiv 55.847 g. of Fe \equiv 40.08 g. of Ca

Chemicals required :

- (1) Standard (M/50) of zinc acetate dihydrate (F.W. 219.38) solution (cf. Experiment No. 1).

$$\text{Strength of Zn-acetate} = \frac{w}{1.0969} (\text{M}/50) = f.(\text{M}/50)$$

where, w = wt. of Zn-acetate dihydrate per 250 ml solution

- (2) (\sim M/50) $\text{Na}_2\text{H}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ (F.W. 372.24) solution (cf. Experiment No. 1).
- (3) 5% Sulfosalicylic acid, or, 5% NH_4SCN indicator (cf. Experiment No. 5).
- (4) EBT indicator (cf. Experiment No. 1).
- (5) Chloroacetic acid buffer (pH = 2.3) (cf. Experiment No. 5)
- (6) NH_3 - NH_4Cl buffer solution of pH 10 (cf. Experiment No. 1).

Procedure :

1. Prepare 250 ml of a standard (M/50) solution of Zn-acetate dihydrate in 2% NH_4Cl solution by accurate weighing.
2. Standardisation of the EDTA solution :

Take an aliquot of 25 ml of the \sim (M/50) EDTA solution, dilute with 20 ml of water, add 5 ml of NH_3 - NH_4Cl buffer solution (pH = 10) and a pinch of EBT indicator. Titrate the mixture with standard (M/50) Zn-acetate solution till the colour changes from blue to wine red. Record the titre (V_1 ml)

3. Estimation of total Fe^{3+} and Ca^{2+} :

Take an aliquot of 25 ml of the mixture, add a measured excess (50 ml say $(25 \times x)$ ml) of standard (\sim M/50 EDTA) solution. Neutralize with 1:1 aqueous NH_3 till smell of NH_3 appears. If there is a brown precipitate due to $\text{Fe}(\text{OH})_3$, add another 25 ml of the standard (\sim M/50) EDTA solution and a few more drops of 1:1 aqueous NH_3 as required to obtain a clear solution smelling NH_3 . Add 10 ml of NH_3 - NH_4Cl buffer (pH=10) and a pinch of EBT indicator. Titrate with (\sim M/50) standard zinc acetate solution till the colour changes from blue to wine red. Record the titre (V_2 ml).

4. Estimation of Fe^{3+} :

Take an aliquot of 25 ml of the mixture, neutralize with 1:1 aqueous NH_3 till a faint turbidity persists in the solution. Add 5 ml of chloroacetic acid buffer ($\text{pH} = 2.3$) and 1 ml of sulfosalicylic acid (or, NH_4SCN) indicator. The solution assumes an intense violet (or, red) colour. Titrate with the standard $\sim(\text{M}/50)$ EDTA solution till the violet (or, red) colour is discharged. Recorded the titre (V_3 ml).

Calculation :

$$25 \times S(\text{EDTA}) = V_1 \times f. (\text{M}/50)$$

$$\therefore S(\text{EDTA}) = (V_1/25) f. (\text{M}/50)$$

$$\begin{aligned} \text{Fe}^{3+} \text{ in 25 ml sample solution} &\equiv V_3 \text{ ml } (V_1/25) f. (\text{M}/50) \text{ EDTA solution} \\ &\equiv (V_1 V_3/25) \text{ ml of } f. (\text{M}/50) \text{ EDTA solution} \end{aligned}$$

$$(25 \times x) \text{ ml of } (V_1/25) f. (\text{M}/50) \text{ EDTA solution}$$

$$\equiv (V_1 \times x) \text{ ml of } f. (\text{M}/50) \text{ Zn}^{2+} \text{ solution}$$

$$\equiv (\text{Fe}^{3+} + \text{Ca}^{2+}) \text{ in 25 ml sample solution} + V_2 \text{ ml of } f. (\text{M}/50) \text{ Zn}^{2+} \text{ solution.}$$

$$\therefore (\text{Fe}^{3+} + \text{Ca}^{2+}) \text{ in 25 ml} \equiv (V_1 x - V_2) \text{ ml of } f. (\text{M}/50) \text{ Zn}^{2+} \text{ solution}$$

$$\equiv (V_1 x - V_2) \text{ ml of } f. (\text{M}/50) \text{ EDTA solution}$$

$$\therefore \text{Ca}^{2+} \text{ in 25 ml} \equiv [(V_1 x - V_2) - (V_1 V_3/25)] \text{ ml of } f. (\text{M}/50) \text{ EDTA solution}$$

$$\therefore 1000 \text{ ml (M) EDTA solution} \equiv 55.847 \text{ g. of Fe} \equiv 40.08 \text{ g. of Ca}$$

$$\therefore \text{Total Fe in 250 ml solution} = \left(\frac{55.847 \times 250}{1000 \times 25 \times 50 \times 25} \right) \times (f. V_1 V_3) \text{ g. of Fe}$$

$$\therefore \text{Total Ca in 250 ml solution} = \frac{40.08 \times 250}{1000 \times 25 \times 50} \times f \times [(V_1 x - V_2) - (V_1 V_3/25)] \text{ g. of Ca}$$

Experiment No. - 9 : Complexometric Estimation of Cu^{2+} in Chalcopyrites

Principles :

Chalcopyrites, CuFeS_2 , is attacked by dil. HNO_3 in presence of H_2O_2 . The resulting solution contains Cu^{2+} and Fe^{3+} . Sulfide is oxidised to sulfur, which is separated. On treatment with aqueous $\sim \text{NH}_3$, Fe^{3+} is precipitated as ferric hydroxide and Cu^{2+} remains in solution in the form of intense blue coloured tetraammine complex, $\text{Cu}(\text{NH}_3)_4^{2+}$. After separation from ferric hydroxide by filtration, copper is estimated in the filtrate by titrating with a standard solution of EDTA at pH 4-5 using PAN indicator.



\therefore 1000 ml of (M) EDTA \equiv 63.54 g. of Cu \equiv 95.604 g. of CuS

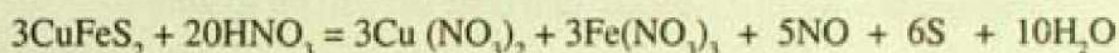
Chemicals required :

- 1) Chalcopyrites ore
- 2) Conc. HNO_3 (A.R)
- 3) Solid NH_4Cl (A.R)
- 4) Acetic acid (A.R)
- 5) '20 Volume' H_2O_2
- 6) Standard (M/50) Zinc acetate solution (cf. Experiment No. 1)
- 7) Standard ~ (M/50) EDTA solution (cf. Experiment No. 1)
- 8) Sodium acetate-acetic acid buffer (pH ~4.5) (cf. Experiment No. 7).
- 9) PAN indicator solution (cf. Experiment No. 7)

Procedure :

1. Dissolution :

Attack ~ 1.0 g of the powdered chalcopyrite with a mixture of 10 ml of water and 3 ml of conc. HNO_3 , heat gently on an asbestos board till dissolution. Add water to replenish the loss of volume of the solution due to evaporation.



The elemental sulfur that is set free, remains suspended in the solution. Dilute the solution with 50 ml of distilled water, cool to room temperature and remove the sulfur particles by filtration (or, with the help of a glass rod, washing accordingly if a globule is formed). Add 10 ml of, "20 Volume" H_2O_2 and warm gently to complete the oxidation of Fe^{II} if any to Fe^{III} , boil for about 10 minutes to decompose the excess H_2O_2 . Cool to room temperature. Filter if necessary and transfer quantitatively into a 250 ml volumetric flask and make the volume up to the mark with distilled water.

2. Separation of iron :

Take an aliquot of 25 ml from the stock solution, dilute with 50 ml of water, add 1 g. of NH_4Cl and bring to boiling. Neutralize with (1:1) aqueous NH_3 solution till the precipitation of Fe^{III} hydroxide is complete and the solution turns intense blue with smell of ammonia. Allow the precipitate to settle, filter through a Whatman No.41 filter paper, wash twice with 1% NH_4Cl solution containing little ammonia. Dissolve the precipitate in 25 ml hot (1:1) HCl , reprecipitate with (1:1) aqueous NH_3 and refilter through the same filter paper as before. Wash the precipitate 3-4 times with 1% NH_4Cl solution containing a little ammonia. Collect the filtrate and the washings for estimation of copper.

3. Standardization of EDTA solution using PAN indicator :

Take an aliquot of 25 ml of the standard (M/50) zinc acetate solution, dilute with 20 ml of water, add 5 ml of acetic acid – acetate buffer solution (pH ~ 4.5). Bring to ~60-70°C, add 2-3 drops of PAN indicator and titrate with (~M/50) EDTA solution till the colour of the solution changes from red to yellow. (titre = V_1 ml)

4. Estimation of Copper :

Boil the combined filtrate and the washings containing copper to remove ammonia, which is indicated by the appearance of a blue precipitate of basic Cu^{II} salts or black precipitate of $\text{Cu}(\text{OH})_2$. Add (1:1) HNO_3 to just dissolve the precipitate and boil down the resulting solution to reduce its volume to ~ 50 ml. Add drops of (1:1) aqueous NH_3 till a faint turbidity appears, then dissolve the turbidity by adding drops of dilute acetic acid. Add 5 ml of sodium acetate-acetic buffer (pH~4.5), 2-3 drops of PAN indicator, when the solution assumes a violet colour. Titrate with standard ~ (M/50) EDTA solution till the colour changes to green. (titre = V_2 ml)

5. Calculate the % of CuS in the sample.

Calculation :

$$\text{Strength of Zn-acetate} = \frac{w}{1.0969} \text{ (M/50)}$$

where, w = wt. of Zn-acetate dihydrate per 250 ml solution.

$$\therefore V_1 \text{ ml of EDTA} \equiv 25 \text{ ml of } \left(\frac{w}{1.0969} \right) \text{ (M/50) } \text{Zn}^{2+}$$

$$\therefore \text{Strength of EDTA} = \frac{25.w}{V_1 \times 1.0969} \text{ (M/50)}$$

$$\therefore 1000 \text{ ml of (M) EDTA} \equiv 63.54 \text{ g. of Cu} \equiv 95.604 \text{ g. of CuS.}$$

$\therefore \text{Cu}^{2+}$ in 25 ml sample solution

$$\equiv V_2 \text{ ml of } \left(\frac{25.w}{V_1 \times 1.0969} \right) \text{ (M/50) EDTA} \equiv \left(\frac{63.54 \times V_2 \times 25 \times w}{1000 \times V_1 \times 1.0969 \times 50} \right) \text{ g. of Cu}$$

$$\equiv 0.02896 \times (wV_2/V_1) \text{ g. of Cu} \equiv \left(\frac{95.604 \times V_2 \times 25 \times w}{1000 \times V_1 \times 1.0969 \times 50} \right) \text{ g. of CuS}$$

$$= 0.04358 \times (wV_2/V_1) \text{ g. of CuS}$$

∴ Total Cu in 250 ml solution

$$= 0.2896 \times (wV_2/V_1) \text{ g. of Cu}$$

Total CuS in 250 ml solution

$$= 0.4358 \times (wV_2/V_1) \text{ g. of CuS}$$

Experiment No. -10 : Complexometric Estimation of Zn^{2+} in Brass

Principle :

Brass (Cu-Zn alloy) is brought into solution by attacking with dil. HNO_3 . As both Cu^{2+} and Zn^{2+} form stable EDTA complexes in the same pH range (4-5), Cu^{2+} has to be removed before proceeding to estimate Zn^{2+} . Cu^{2+} may be separated as sparingly soluble CuS or CuSCN . Zn^{2+} may then be estimated in the filtrate by titrating with a standard solution of EDTA either at pH 4.5 using PAN indicator or at pH 10 using EBT indicator. Zn^{2+} forms 1:1 complex with EDTA.



$$\therefore \text{EDTA} \equiv \text{Zn}$$

$$\therefore 1000 \text{ ml of (M) EDTA solution} \equiv 65.38 \text{ g. of Zn}$$

Chemicals required :

- 1) Brass sample
- 2) Standard (M/50) zinc acetate solution to be prepared by accurate weighing (cf. Experiment No. 1)
- 3) ~-(M/50) EDTA solution (cf. Experiment No. 1)
- 4) Conc. HNO_3 (A.R)
- 5) 4(N) H_2SO_4 (A.R)
- 6) 10% NH_4SCN solution
- 7) 10% NaOH solution
- 8) Solid Na_2SO_3
- 9) EBT indicator (cf. Experiment No. 1)
- 10) PAN indicator solution (cf. Experiment No. 7)
- 11) Acetate buffer (pH 4.5) : Mix equal volumes of each of 0.5 (M) sodium acetate and 0.5 (M) acetic acid.
- 12) NH_4Cl - NH_3 buffer solution of pH 10 (cf. Experiment No. 1)

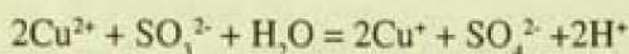
Procedure :

1. Dissolution :

Attack ~ 0.5 g (w^t g. say) of the alloy with a mixture of 15 ml water and 5 ml of conc. HNO₃. Warm gently on an asbestos board till dissolution. Cool, and add ~ 50 ml of water, boil for 2-3 minutes to dissolve all soluble salts.

2. Separation of Cu :

Cool the resulting solution to room temperature, neutralise with dil. 10% NaOH solution till a faint turbidity persists in the solution. Add drops of dil. H₂SO₄ to just dissolve the turbidity, and finally add 5 ml of 4(N) H₂SO₄ and dilute to 100 ml to adjust the acidity to ~0.2(N). Heat nearly to boiling and add solid Na₂SO₃ to reduce Cu^{II} to Cu^I, which is indicated by discharge of blue colour of Cu²⁺.



At this stage, add 10 ml of 10% NH₄SCN solution to completely precipitate Cu^I as CuSCN. Avoid large excess of NH₄SCN, as this may increase the solubility of CuSCN due to complex formation. Allow the mixture to stand for half an hour, add a few more drops of NH₄SCN solution to the clear supernatant liquid to ensure complete precipitation of CuSCN. Then filter the precipitate through a suction filter using a G-4 sintered crucible or through an asbestos bed. [Keep the precipitate of CuSCN always covered with the solution containing sulfite to prevent aerial oxidation of Cu^I to Cu²⁺, which is indicated by the appearance of turbidity in the filtrate]. Wash 3-4 time with 1% Na₂SO₃ solution containing 1.0 g NH₄SCN per 100 ml and a few drops of dil. H₂SO₄ to ensure complete draining of Zn²⁺ into the filtrate. Boil the combined filtrate and washings for ~10 minutes to remove SO₂, cool to room temperature, transfer into a 250 ml volumetric flask and make the volume up to the mark with distilled water.

3.(a) Estimation of Zn using PAN indicator :

Take an aliquot of 25 ml from the prepared stock solution, neutralize with (1:1) aqueous NH₃ till a faint permanent turbidity persists in the solution. Dissolve the turbidity by adding drops of dil. acetic acid, then add 5 ml of sodium acetate – acetic acid buffer (pH ~ 4.5), warm to 60-70°C, and add 3-4 drops of PAN indicator. The solution assumes a red colour. Titrate with standard (~M/50) EDTA solution till the colour of the solution changes from red to yellow. (titre = V ml)

(b) Standardise the EDTA solution against standard zinc acetate using PAN indicator at pH ~ 4.5 following the same procedure. (titre = V' ml)

4.(a) Estimation of Zn using EBT indicator :

To an aliquot of 25 ml of the prepared solution add (1:1) aqueous NH₃ till smell of

NH_3 appears. Add 5 ml of $\text{NH}_4\text{Cl}-\text{NH}_3$ buffer (pH~10) and a pinch of EBT indicator. The solution assumes a wine red colour. Titrate with standard ~ (M/50) EDTA solution till the colour of the solution changes from wine red to blue. (titre = V ml)

(b) Standardise the EDTA solution against standard zinc acetate using EBT indicator at pH 10 following the same procedure. (titre = V' ml)

6. Calculate the % of Zn in the brass sample.

Calculation :

$$\text{Strength of Zn-acetate} = \frac{w}{1.0969} \text{ (M/50)}$$

where, w = wt. of Zn-acetate dihydrate in 250 ml solution.

$$\therefore V' \text{ ml of EDTA} \equiv 25 \text{ ml of } \left(\frac{w}{1.0969} \right) \text{ (M/50) } \text{Zn}^{2+}$$

$$\therefore \text{Strength of EDTA} = \left(\frac{25 \times w}{V' \times 1.0969} \right) \text{ (M/50)}$$

$$\therefore 1000 \text{ ml of (M) EDTA} \equiv 65.38 \text{ g. of Zn.}$$

$$\therefore \text{Zn}^{2+} \text{ in 25 ml of sample solution}$$

$$= V \text{ ml of } \left(\frac{25 \times w}{V' \times 1.0969} \right) \text{ (M/50) EDTA}$$

$$= \left(\frac{65.38 \times V \times 25 \times w}{1000 \times V' \times 1.0969 \times 50} \right) \text{ g. of Zn}$$

$$= 0.0298 \times (w V/V') \text{ g. of Zn}$$

$$\therefore \text{Total Zn in 250 ml of sample solution}$$

$$= 0.298 \times (w V/V') \text{ g.}$$

$$\therefore \% \text{ of Zn in the brass sample}$$

$$= 0.298 \times \left(\frac{wV}{V'w'} \right) \times 100\%$$

$$= 29.8 \times \left(\frac{wV}{w'V'} \right) \%$$

Chapter – 7

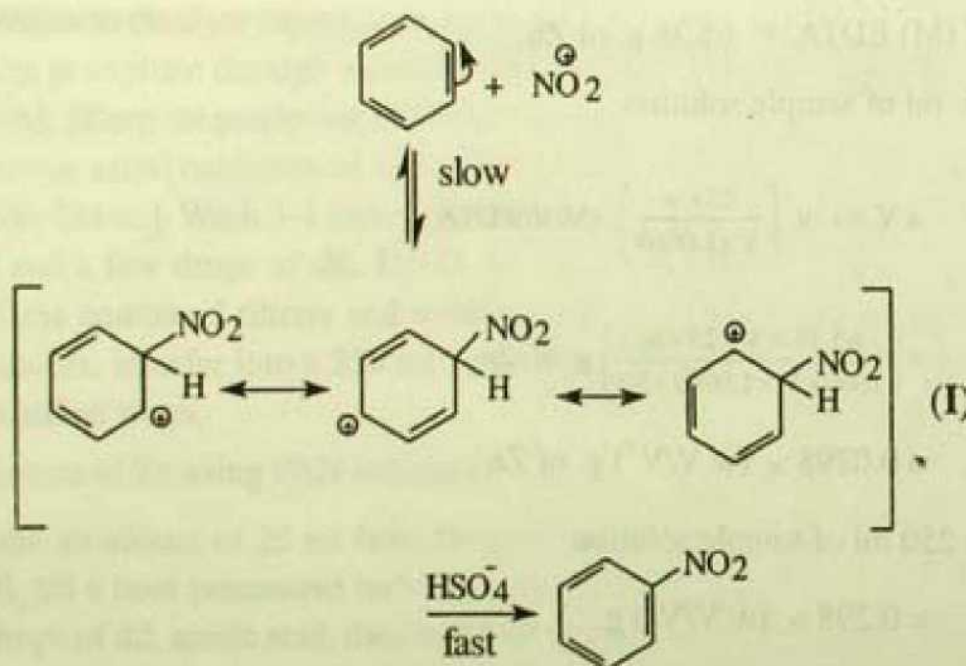
Organic Reactions

1. Nitration of aromatic compounds

Aromatic hydrocarbons may be nitrated with concentrated nitric acid in presence of concentrated sulphuric acid ('mixed acid reagent'). The function of sulphuric acid is to assist the formation of nitronium ion, NO_2^+ , which is the effective nitrating agent :

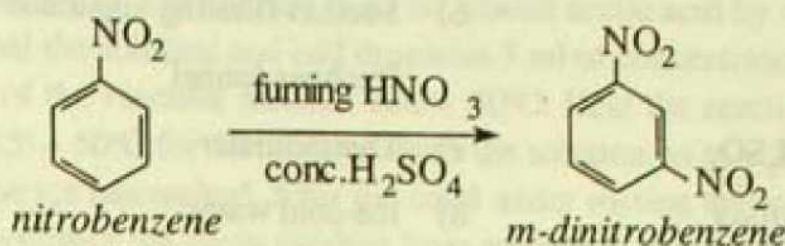


The mechanism of nitration is a two-step process involving electrophilic attack of the nitronium ion on an aromatic nucleus to form the intermediate mesomeric ion (I) (σ -complex) followed by removal of a proton by the hydrogensulphate (HSO_4^-) ion :



Nitration of aromatic hydrocarbons with mixed acid reagent usually occurs at comparatively low temperature whereas nitration of aromatic compounds containing an electron withdrawing group (e.g., $-\text{NO}_2$, $-\text{SO}_3\text{H}$, $-\text{CHO}$, $-\text{CO}_2\text{H}$ etc.) occur under forcing condition requiring the use of fuming nitric acid and concentrated sulphuric acid and a higher temperature.

Experiment No. 1 : Preparation of *m*-dinitrobenzene



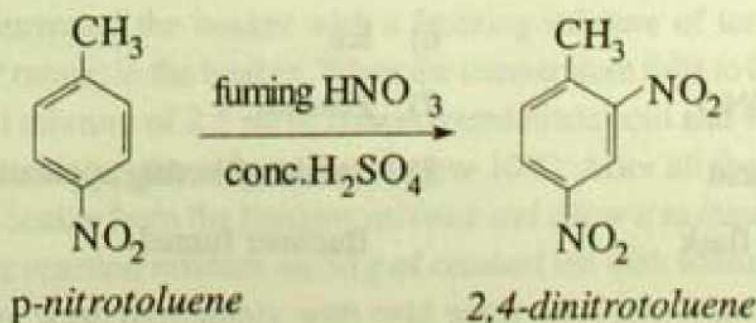
Chemicals and apparatus required :

- | | |
|--------------------------------|-------------------------------------|
| 1) Nitrobenzene | 6) Suction filtering apparatus with |
| 2) Fuming nitric acid | Buchner funnel. |
| 3) Concentrated sulphuric acid | 7) Hot water bath. |
| 4) 100 ml round-bottomed flask | 8) Ice-cold water. |
| 5) Air condenser | 9) Rectified spirit |

Procedure :

Place 7 ml of concentrated sulphuric acid and 5 ml of fuming nitric acid in a 100 ml dry conical flask. Add a few pieces of boiling chips. Then add 4 ml of nitrobenzene in portions of about 1 ml to the liquid into the conical flask; after each addition shake the flask well to ensure thorough mixing of the liquids. Attach an air condenser at the mouth of the flask and heat the mixture on a boiling water bath with frequent shaking for 30 minutes (or until a drop of the reaction mixture readily solidifies on pouring into cold water taken in a test tube). Allow the mixture to cool somewhat and pour it cautiously with vigorous stirring into about 100 ml of ice-cold water. Filter the solid under suction, wash thoroughly with cold water until the washings are acid-free, drain well, dry in air. Recrystallise the crude product from rectified spirit (~ 30 ml). The yield of the pale yellow crystals of *m*-dinitrobenzene, is 5 g. and its m.p. is 89° – 90°C.

Experiment No. – 2 : Preparation of 2,4-dinitrotoluene



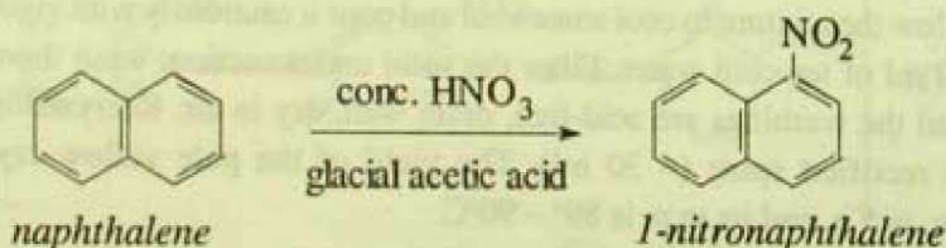
Chemicals and Apparatus required :

- | | |
|---|-------------------------------------|
| 1) <i>p</i> -Nitrotoluene | 6) Suction filtering apparatus with |
| 2) Fuming HNO_3 | Buchner funnel |
| 3) Concentrated H_2SO_4 | 7) Thermometer |
| 4) 100 ml conical flask | 8) Ice-cold water |
| 5) Hot water bath | 9) Methanol |

Procedure :

Place 3 ml of fuming nitric acid and 4 ml of concentrated sulphuric acid and a few pieces of unglazed porcelain in a 100 ml dry conical flask. Add gradually, in small portions, 3.5 g of *p*-nitrotoluene into the acid mixture keeping the temperature of the reaction mixture below 50°C . Cool the flask if necessary by immersing in cold water. Place a small funnel at the mouth of the flask and heat on a water bath at $90^\circ - 95^\circ\text{C}$ for 30 minutes. Allow to cool to laboratory temperature and pour the reaction mixture slowly into 125 ml ice-cold water. Filter the crude 2,4-dinitrotoluene under suction, wash thoroughly with cold water and drain well. Recrystallise from minimum volume of hot methanol. The yield of pure 2,4-dinitrotoluene, is ~ 3 g. and its m.p. is 71°C .

Experiment No. -3 : Preparation of 1-nitronaphthalene



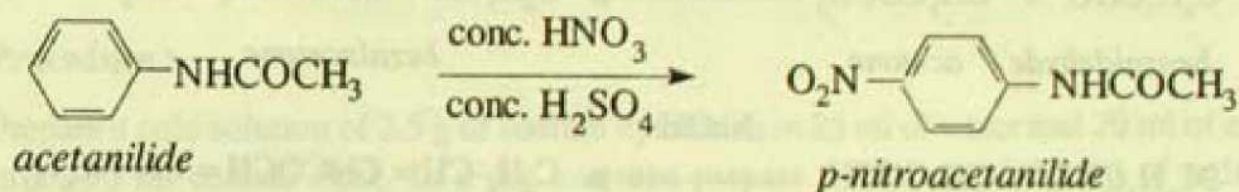
Chemicals & Apparatus required

- | | |
|--------------------------------|-------------------------------------|
| 1) Naphthalene | 6) Ice |
| 2) Concentrated HNO_3 | 7) Ethanol |
| 3) Glacial acetic acid | 8) Suction filtering apparatus with |
| 4) 100 ml conical flask | Buchner funnel. |
| 5) Thermometer | |

Procedure

Dissolve 3 g of naphthalene in 15 ml glacial acetic acid by warming in a 100 ml conical flask. Cool the solution and add dropwise 3 ml of concentrated nitric acid keeping the temperature of the reaction mixture below 40°C. Heat the reaction mixture on a hot water bath at ~ 45° – 50°C for 10 minutes. Pour the solution on to ~ 20 g crushed ice with stirring. When the ice has melted, filter the solid under suction and wash thoroughly with cold water. Recrystallise the crude product from ethanol. 1-Nitronaphthalene separates as, pale yellow needles of m.p. 61°C. The yield is ~3.5 g.

Experiment No. - 4 : Preparation of *p*-nitroacetanilide



Chemicals and Apparatus required

- | | |
|--|-------------------------------------|
| 1) Acetanilide | 6) Ice-salt freezing mixture |
| 2) Concentrated HNO ₃ | 7) Thermometer |
| 3) Concentrated H ₂ SO ₄ | 8) Rectified spirit |
| 4) Glacial acetic acid | 9) Suction filtering apparatus with |
| 5) 100 ml beaker | Buchner funnel |

Procedure

Place 5 ml of glacial acetic acid and 5 g of acetanilide in a dry 100 ml beaker. Add 10 ml concentrated sulphuric acid with stirring. The mixture becomes warm and a clear solution results. Surround the beaker with a freezing mixture of ice and salt and place a thermometer (110° range) in the beaker. When the temperature falls to 0° – 2°C, add dropwise with stirring a cold mixture of 2.5 ml of concentrated nitric acid and 1.5 ml of concentrated sulphuric acid maintaining the temperature below 10°C. After all the mixed acid has been added, remove the beaker from the freezing mixture and allow it to stand at room temperature for 1 hour. Pour the reaction mixture on 50 g of crushed ice with stirring. Filter the resulting solid under suction, wash thoroughly with cold water until free from acids and drain well.

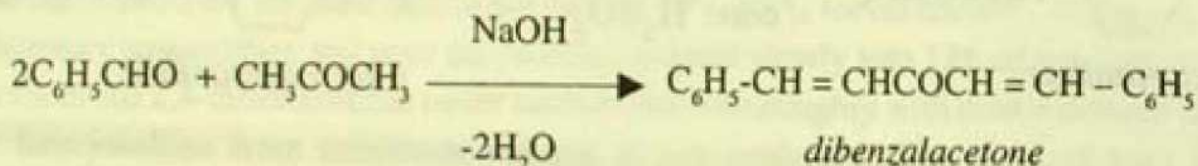
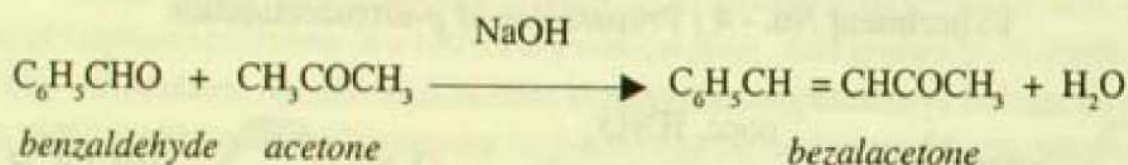
Recrystallise the pale yellow product from rectified spirit, wash with little cold alcohol and dry in air upon filter paper. *p*-Nitroacetanilide appears as colourless crystals of m.p. 214°C.

The yield is ~ 4 g.

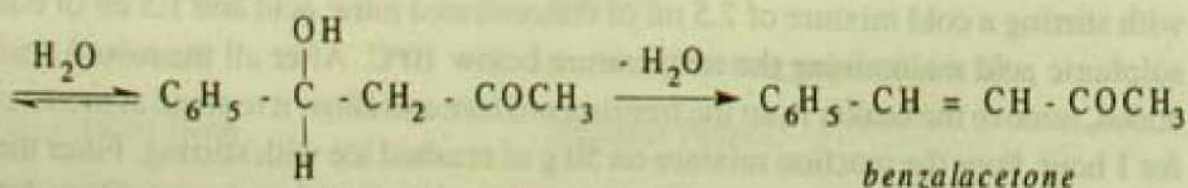
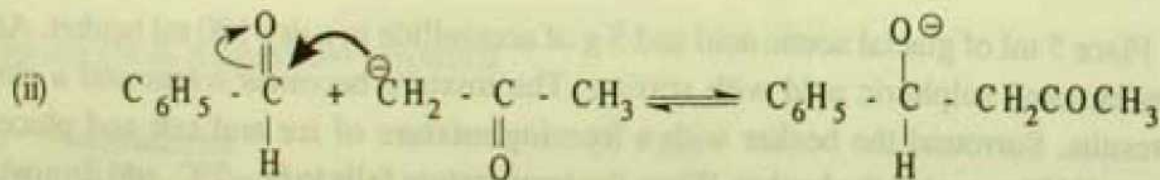
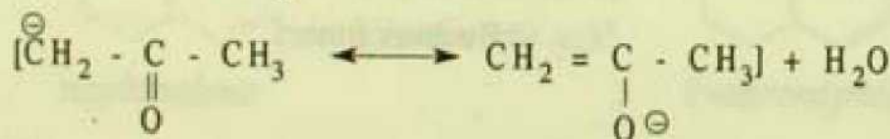
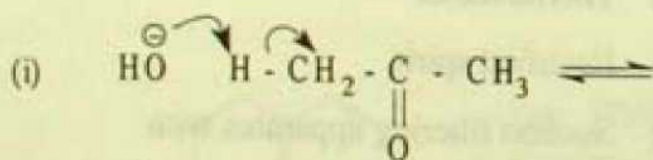
2. Condensation reactions involving elimination of H₂O/NH₃

Claisen-Schmidt Reaction

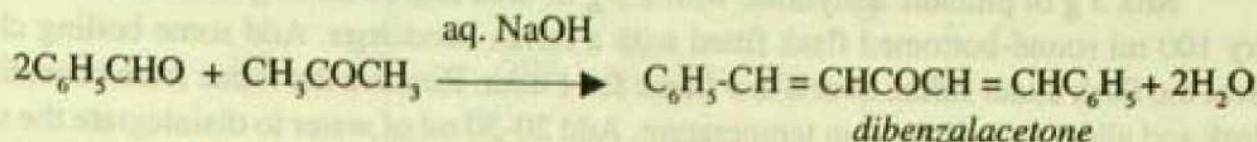
α , β -Unsaturated keto-compounds may be synthesised by the condensation of an aromatic aldehyde with an aliphatic aldehyde, ketone- or nitro-compound containing an active α -methylene group in presence of alkali :



Mechanism : The initial step involves the formation of a carbanion followed by its nucleophilic addition on the carbonyl group of the aromatic aldehyde.



Experiment No. - 5 : Preparation of dibenzalacetone



Chemicals and Apparatus required

- | | |
|-------------------------|-------------------------------------|
| 1) Benzaldehyde | 6) Ice |
| 2) Acetone | 7) Thermometer |
| 3) Ethyl alcohol | 8) Rectified spirit |
| 4) Sodium hydroxide | 9) Suction filtering apparatus with |
| 5) 150 ml conical flask | Buchner funnel |

Procedure :

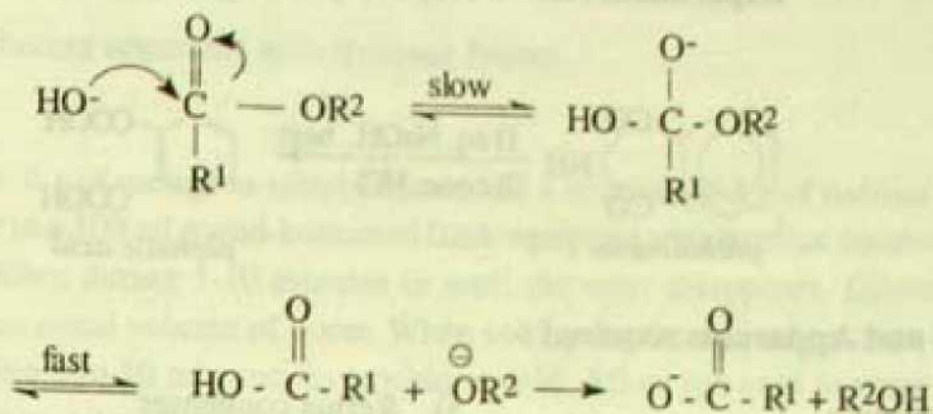
Prepare a cold solution of 2.5 g of sodium hydroxide in 25 ml of water and 20 ml of ethanol in a 150 ml conical flask. In a dry test tube prepare a mixture of 2.5 ml of redistilled benzaldehyde and 1 ml of A.R. acetone. Add the mixture from the test tube into the cold solution in the conical flask. Shake frequently and keep the temperature at 20-25°C for 15 minutes by immersing the flask in a bath of ice cold water. Collect the precipitated dibenzalacetone by filtration at the pump, wash with cold water to remove the alkali and dry the solid at room temperature upon the filter paper. Recrystallise the crude product from hot rectified spirit. Dibenzalacetone appears as pale yellow crystalline needles, m.p. 112°C. The yield is ~ 2.2 g.

Experiment No. - 6 : Preparation of phthalimide

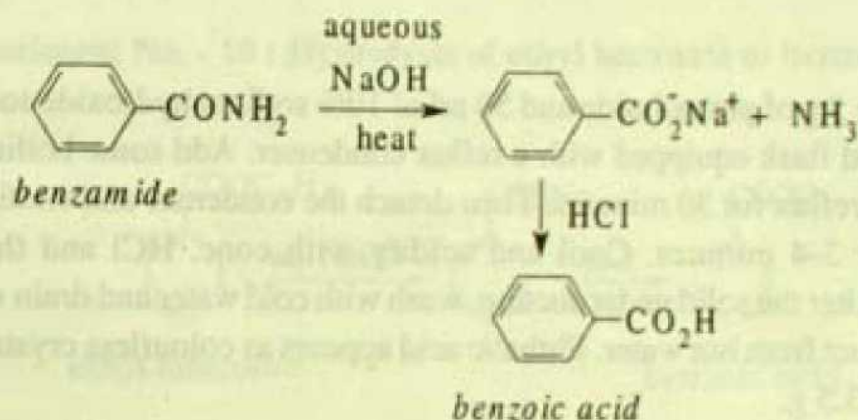


Chemical and Apparatus required :

- 1) Phthalic anhydride
- 2) Urea
- 3) Acetic acid
- 4) 100 ml R.B. flask
- 5) Reflux condenser
- 6) Rectified spirit
- 7) Suction filtering apparatus with Buchner funnel



Experiment No. - 7 : Hydrolysis of benzamide



Chemicals and Apparatus required :

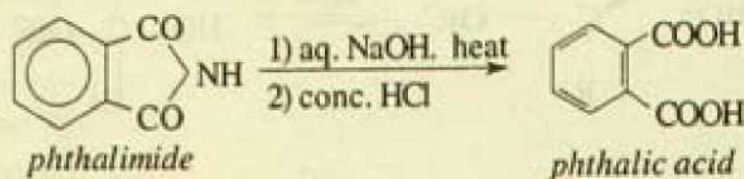
- | | |
|----------------------------|-------------------------------------|
| 1) Benzamide | 5) Reflux condenser |
| 2) Sodium hydroxide (10%) | 6) Suction filtering apparatus with |
| 3) Conc. Hydrochloric acid | Buchner funnel |
| 4) 150 ml R.B. flask | |

Procedure :

Place 5 g of benzamide and 50 ml of 10% sodium hydroxide solution in a 150 ml round-bottomed flask equipped with a reflux condenser. Add some boiling chips. Boil the mixture under reflux for 30 minutes. Then detach the condenser and continue boiling in the open flask for 3-4 minutes. Cool and acidify with conc. HCl and then allow to stand at room temperature. Filter the resulting solid under suction, wash with cold water and drain well.

- Recrystallise the crude product from hot water. Benzoic acid appears as colourless crystals of m.p. 122°C. The yield is 3 g.

Experiment No. - 8 : Hydrolysis of phthalimide



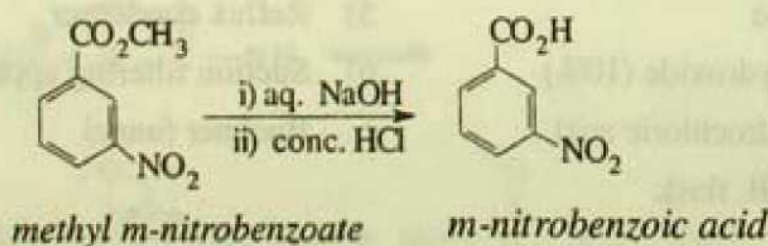
Chemical and Apparatus required :

- | | |
|----------------------------|--------------------------------------|
| 1) Phthalimide | 5) Reflux condenser |
| 2) Sodium hydroxide (10%) | 6) Suction filtering apparatus using |
| 3) Conc. Hydrochloric acid | Buchner funnel |
| 4) 150 ml R.B. flask | |

Procedure :

Place 5 g of phthalimide and 50 ml of 10% sodium hydroxide solution in a 150 ml round bottomed flask equipped with a reflux condenser. Add some boiling chips. Boil the mixture under reflux for 30 minutes. Then detach the condenser and continue boiling in the open flask for 3-4 minutes. Cool and acidify with conc. HCl and then cool to room temperature. Filter the solid under suction, wash with cold water and drain well. Recrystallise the crude product from hot water. Phthalic acid appears as colourless crystals of m.p. 195°C. The yield is ~ 3.5 g.

Experiment No. - 9 : Hydrolysis of methyl *m*-nitrobenzoate



Chemicals and Apparatus required :

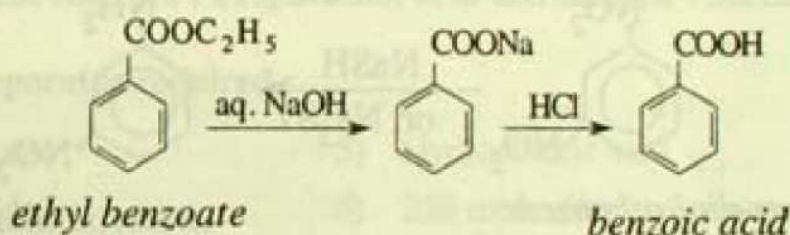
- 1) Methyl *m*-nitrobenzoate
- 2) Sodium hydroxide
- 3) Concentrated Hydrochloric acid
- 4) 100 ml R.B. flask

- 5) Reflux condenser
- 6) Suction filtering apparatus with Buchner funnel

Procedure :

Place 6 g of methyl *m*-nitrobenzoate and a solution of 3 g of sodium hydroxide in 15 ml of water in a 100 ml round-bottomed flask equipped with a reflux condenser. Heat the mixture to boiling during 5-10 minutes or until the ester disappears. Dilute the reaction mixture with an equal volume of water. When cold, pour the diluted reaction mixture with vigorous stirring into 10 ml conc. hydrochloric acid. Allow to cool to room temperature, filter the crude *m*-nitrobenzoic acid at the pump and wash it with water, dry on a steam bath. Recrystallise the crude *m*-nitrobenzoic acid from 1 per cent hydrochloric acid. The pure acid is a pale cream solid of m.p. 141°C. The yield is ~5.5 g.

Experiment No. - 10 : Hydrolysis of ethyl benzoate to benzoic acid



Chemicals and Apparatus required :

- | | |
|---------------------------|-------------------------------------|
| 1) Ethyl benzoate | 5) Reflux |
| 2) Sodium hydroxide (20%) | 6) Suction filtering apparatus with |
| 3) Hydrochloric acid | Buchner funnel |
| 4) 150 ml R.B. flask | |

Procedure :

Place 5 ml of ethyl benzoate and 50 ml of 20% sodium hydroxide solution in a 150 ml round-bottomed flask equipped with a reflux condenser. Add some boiling chips. Boil the mixture under reflux for 45 minutes or until the ester layer disappears. Cool and acidify with conc. HCl and then allow to stand at room temperature. Filter the crude benzoic acid under suction, wash with cold water and drain well. Recrystallise the crude acid from hot water. Pure benzoic acid separates as colourless crystals of m.p. 122°C. The yield is ~ 2.5 g.

Note : Reaction times required for complete hydrolysis of some common esters with 20% NaOH solution are : Methyl benzoate – 30 min, Ethyl phthalate – 1 hr., Methyl salicylate – 15-20 min.

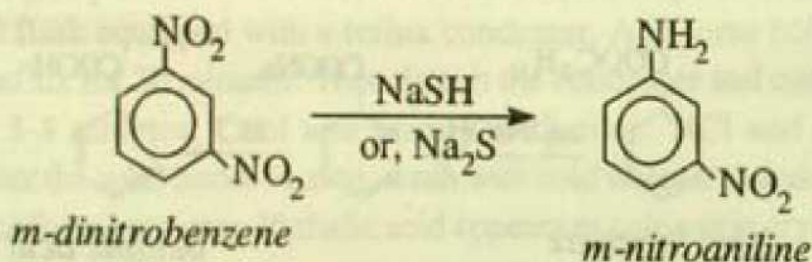
4. Reduction

(a) Reduction of aromatic nitro compounds

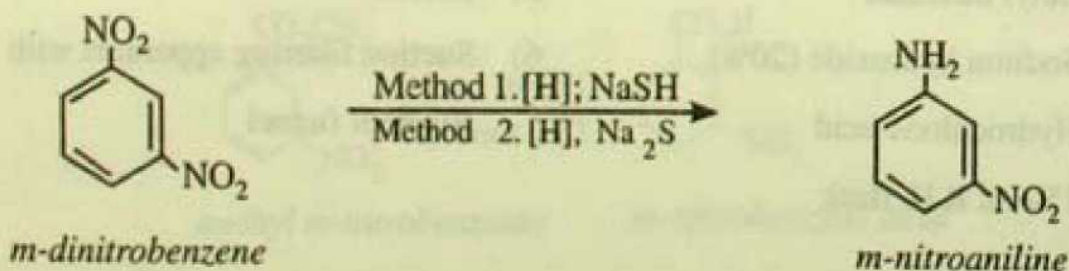
Primary arylamines are generally prepared by reduction of aromatic nitro compounds with metal-acid (Sn/HCl or Fe/HCl).



In case of *m*-dinitrobenzene, one nitro group can be selectively reduced by sodium sulphide, or, sodium hydrogen sulphide.



Experiment No. - 11 : Preparation of *m*-nitroaniline : Method – I



Chemicals and Apparatus required :

- | | |
|-----------------------|-------------------------------------|
| 1) Sodium Sulphide | 5) Reflux condenser |
| 2) Sodium bicarbonate | 6) Suction filtering apparatus with |
| 3) Methanol | Buchner funnel |
| 4) 250 ml R.B. flask | |

Procedure :

(a) Preparation of NaSH solution : Dissolve 12 g. of crystallised sodium sulphide in 33 ml of water; add 4 g of finely powdered sodium bicarbonate in small portions with stirring. When the bicarbonate has dissolved completely, add 33 ml of methanol and cool below 20°C. Filter off the precipitated sodium carbonate at the pump, wash the precipitate with methanol (3 x 5 ml). Retain the filtrate and the washings. These contain about 2.6 g of NaSH in solution which is used for the reduction.

(b) Reduction of *m*-dinitrobenzene : Dissolve 4.4 g of *m*-dinitrobenzene in 35 ml of hot methanol in a 250 ml round-bottomed flask and add with shaking the previously prepared methanolic solution of NaSH. Attach a reflux condenser and boil the mixture for 20 minutes (ignore any further precipitate of sodium carbonate which may appear). Allow the reaction mixture to cool and fit the condenser for distillation. Distill off most of the methanol (60 – 80 ml) from a water bath. Pour the liquid residue with stirring into about 130 ml of cold water. Collect the bright yellow crystals of *m*-nitroaniline under suction, wash with water and recrystallise from 75 per cent aqueous methanol. The yield is ~ 2.7 g. and its m.p. is 114°C.

Experiment No. – 12 : Preparation of *m*-nitroaniline : Method – 2 :

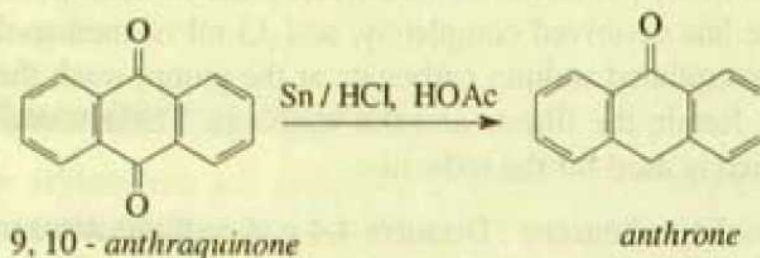
Chemicals and Apparatus required :

- | | |
|-----------------------------|-------------------------------------|
| 1) <i>m</i> -Dinitrobenzene | 5) Hydrochloric acid |
| 2) Sodium sulphide | 6) 250 ml beaker (two pieces) |
| 3) Sulphur powder | 7) Suction filtering apparatus with |
| 4) Ammonia solution | Buchner funnel |

Prepare a solution of sodium polysulphide by dissolving 10 g of crystallised sodium sulphide, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ in 40 ml of water, adding 2.5 g of finely powdered sulphur and warming until a clear solution is produced. Heat a mixture of 6 g of *m*-dinitrobenzene and 50 ml of water contained in a 250 ml beaker until the water boils gently; stir the solution with a glass rod. Place the sodium polysulphide solution in a dropping funnel so that the end of the stem is immediately above the solution in the beaker. Add sodium polysulphide solution during 30 minutes to the vigorously stirred, boiling mixture and boil gently for a further 20 minutes. Allow to cool by adding some ice. Filter the solid product at the pump and wash with cold water. Transfer the solid in to a 250 ml beaker containing 40 ml of water and 9 ml of conc. HCl and boil for 15 minutes when the *m*-nitroaniline dissolves leaving any unreacted sulphur and any unchanged *m*-dinitrobenzene. Filter, and to the filtrate add an excess of conc. aqueous ammonia to precipitate the *m*-nitroaniline. Filter the product and recrystallise it from boiling water. *m*-Nitroaniline, appears as bright yellow needles of m.p. 114°C. The yield is ~3 g.

(b) Reduction of carbonyl compounds

Experiment No. — 13 : Preparation of Anthrone



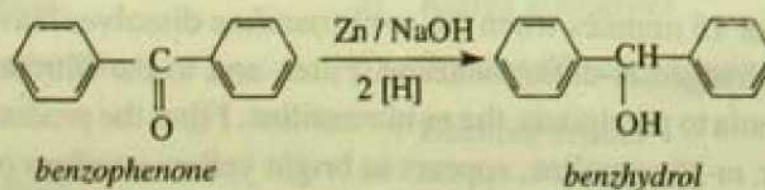
Chemicals and Apparatus required :

- | | |
|-----------------------------------|-------------------------------------|
| 1) Anthraquinone | 6) Reflux condenser |
| 2) Granulated tin | 7) Thermometer |
| 3) Glacial acetic acid | 8) Suction filtering apparatus with |
| 4) Concentrated hydrochloric acid | Buchner funnel |
| 5) 100 ml R.B. flask | |

Procedure :

Place 5 g of anthraquinone, 5 g of granulated tin and 40 ml of glacial acetic acid in a 100 ml round-bottomed flask equipped with a reflux condenser. Heat the mixture to the boiling point and gradually add 13 ml of conc. hydrochloric acid during 15 minutes through the top of the condenser to the boiling solution. Keep the mixture gently boiling under reflux until the solid anthraquinone has completely dissolved (if some solid remains undissolved add more tin and hydrochloric acid). Continue boiling for a further half an hour. Filter the hot solution under suction and add ~ 5 ml water to the filtrate. Cool the solution to about 10°C, collect the crystalline anthrone by filtration at the pump and wash with water. Recrystallise it from a benzene – light petrol (60° – 80°) (3:1) mixture. The yield of pure anthrone, is ~ 3 g. Its m.p. is 155°C.

Experiment No. – 14 : Preparation of benzhydrol



Chemicals and Apparatus required :

- | | |
|-------------------------------|-------------------------------------|
| 1) Benzophenone | 6) 150 ml R.B. flask |
| 2) Zinc dust | 7) Reflux condenser |
| 3) Sodium hydroxide | 8) Suction filtering apparatus with |
| 4) Ethanol (Rectified spirit) | Buchner funnel |
| 5) Hydrochloric acid | |

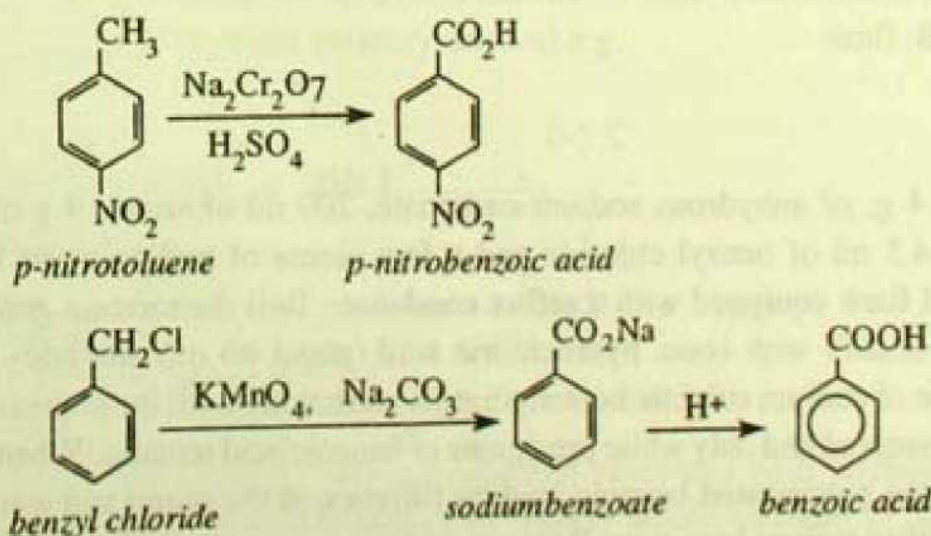
Procedure :

Place 5 g of benzophenone, 55 ml of rectified spirit, 6.5 g of sodium hydroxide and 6.5 g of zinc dust in a 150 ml round-bottomed flask fitted with a reflux condenser. Thoroughly mix the contents of the flask by swirling and then gently boil the mixture under reflux on a water bath for one and a half-hours. Filter the hot solution under suction and pour the filtrate into 225 ml of ice-water containing 12 ml conc. hydrochloric acid. After standing for some time, the product separates as a crystalline solid. Filter the solid at the pump, wash with water. Recrystallise it from hot rectified spirit. Pure benzhydrol appears as colourless crystals of m.p. 68°C. The yield is ~ 3 g.

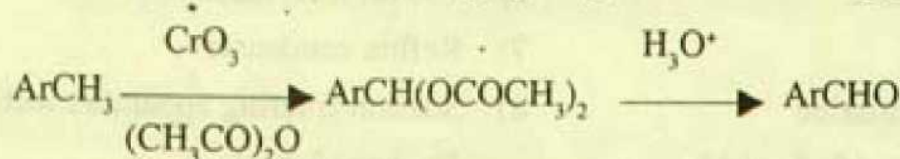
5. Oxidation

Oxidation of a side chain attached to an aromatic compounds :

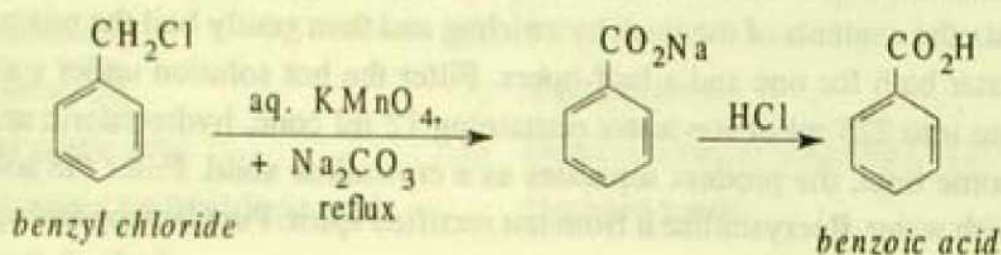
Oxidation of an alkyl group or a halogenated alkyl group attached to an aromatic system is a frequently used method for the preparation of the corresponding carboxylic acids. Oxidation can be accomplished by using either a solution of sodium dichromate in sulphuric acid or aqueous alkaline (or neutral) potassium permanganate solution.



Methyl group can be selectively oxidised to $-\text{CHO}$ group by chromium trioxide in acetic anhydride and acetic acid medium followed by hydrolysis of the resulting *gem*-diacetate.



Experiment No. - 15 : Preparation of benzoic acid



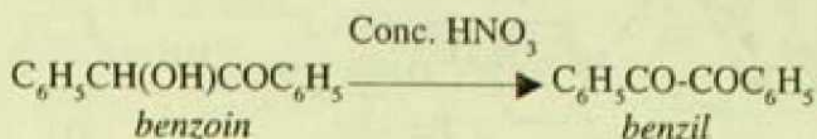
Chemicals and Apparatus required :

- | | |
|-------------------------------|-------------------------------------|
| 1) Benzyl chloride | 6) Reflux condenser |
| 2) Anhydrous sodium carbonate | 7) Sodium sulphite heptahydrate |
| 3) Potassium permanganate | 8) Suction filtering apparatus with |
| 4) Hydrochloric acid | Buchner funnel |
| 5) 500 ml R.B. flask | |

Procedure :

Place 4 g. of anhydrous sodium carbonate, 200 ml of water, 9 g of potassium permanganate, 4.5 ml of benzyl chloride and a few pieces of boiling chips in a 500 ml round-bottomed flask equipped with a reflux condenser. Boil the mixture gently for 1 hr. Allow to cool, acidify with conc. hydrochloric acid (about 40 ml) and add 20 per cent aqueous solution of sodium sulphite heptahydrate with shaking until the manganese dioxide is completely dissolved and only white precipitate of benzoic acid remains. When the mixture is cold, collect the precipitated benzoic acid by filtration at the pump and wash with cold water. Recrystallise it from hot water. Benzoic acid appears as colourless crystals of m.p. 122°C . The yield is ~ 3.5 g.

Experiment No. – 16 : Preparation of benzil



Chemicals and Apparatus required :

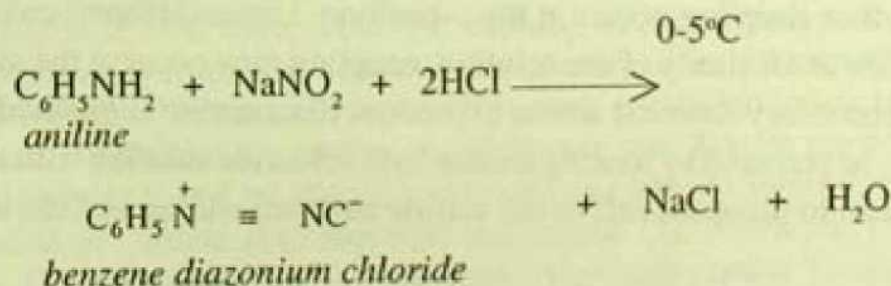
- 1) Benzoin
- 2) Concentrated Nitric acid
- 3) Rectified spirit
- 4) 100 ml R.B. flask
- 5) Suction filtering apparatus with Buchner funnel

Procedure :

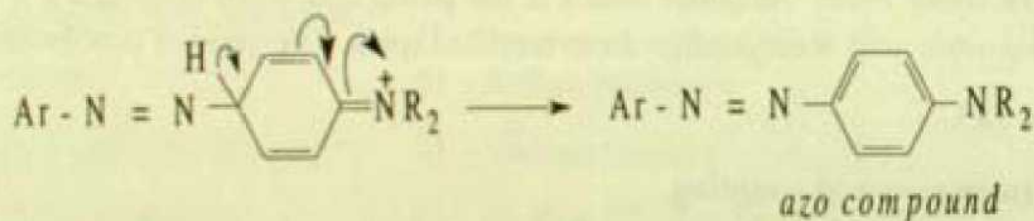
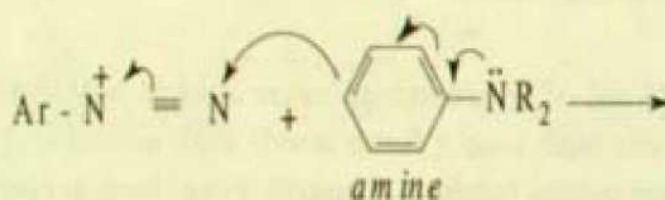
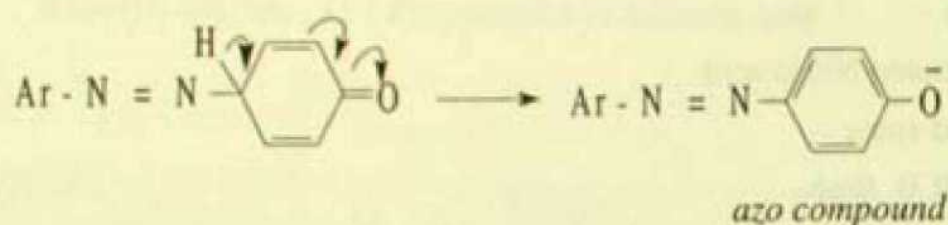
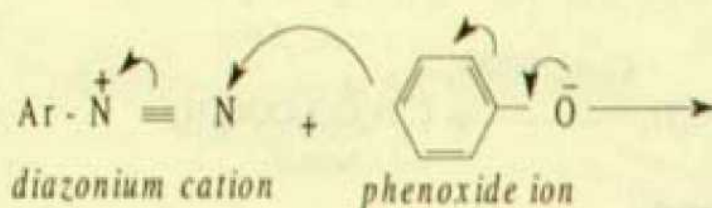
Place 5 g of benzoin and 25 ml of concentrated nitric acid in a 100 ml round-bottomed flask. Heat on a boiling water bath (use a fume hood) with occasional shaking until the evolution of oxides of nitrogen ceases (about 1.5 hours). Pour the reaction mixture into 75-100 ml of cold water contained in a beaker, stir well until the oil crystallises completely as a yellow solid. Filter the crude benzil at the pump and wash thoroughly with water to remove the nitric acid. Recrystallise from rectified spirit. The yield of pure benzil is ~ 4.5 g. Its m.p. is 95°C.

6. Diazotization and coupling

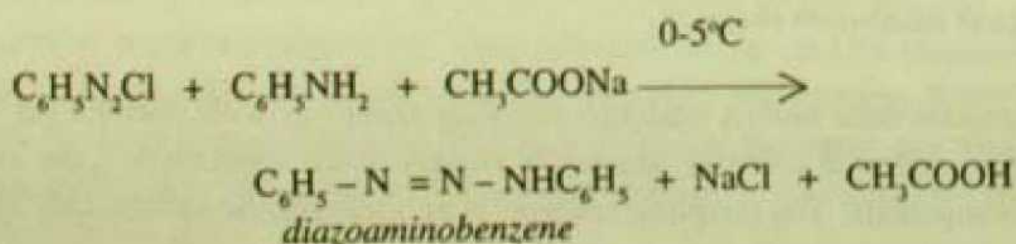
Aromatic primary amines react with nitrous acid in the presence of hydrochloric acid (or other mineral acid) at 0° – 5°C to yield diazonium salts. This reaction is called *diazo reaction* (diazotization of aromatic primary amines) e.g.,



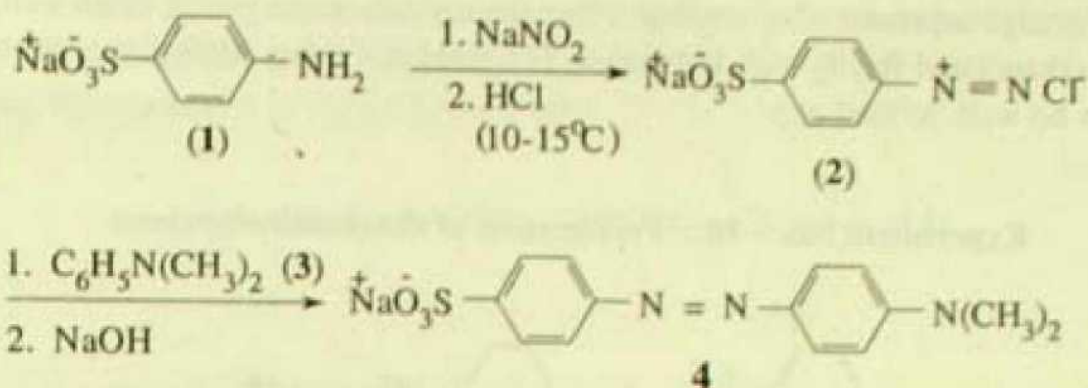
Diazonium salts readily undergo *coupling reactions* with phenols (in weakly alkaline medium) and with aromatic amines in weakly acidic medium to form intensely coloured azo-compounds. The coupling reaction is an electrophilic substitution in which the electrophile is the phenoxide ion, or, the free amine.



Coupling occurs preferentially in the *p*-position to the hydroxyl or the amino group, but if this position is blocked, then coupling occurs at the *o*-position. Under different conditions depending upon the acidity or alkalinity of the solution, coupling may occur at the nitrogen atom of a primary, or, a secondary aromatic amine to produce diazoamino compounds, e.g., diazoaminobenzene may be prepared by treating aniline hydrochloride solution with sodium nitrite, that is just sufficient to diazotise half of the aniline and then adding sodium acetate.



Experiment No. - 17 : Preparation of methyl orange



Chemicals & Apparatus required :

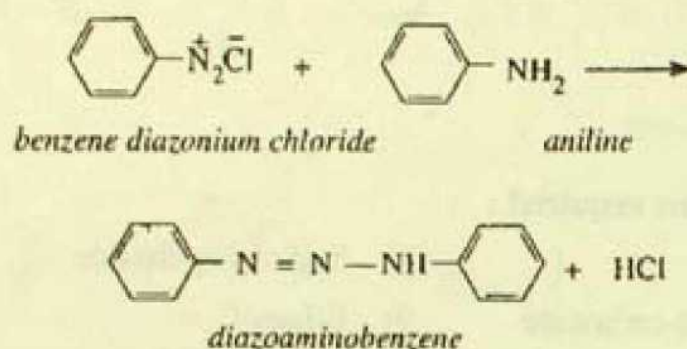
- | | |
|-------------------------------|--|
| 1) Sulphanilic acid | 8) Sodium hydroxide |
| 2) Anhydrous sodium carbonate | 9) Ethanol |
| 3) Sodium nitrite | 10) Ether |
| 4) Conc. hydrochloric acid | 11) Ice |
| 5) Dimethylaniline | 12) Beaker (500 ml, 250 ml) |
| 6) Glacial acetic acid | 13) Thermometer (0° – 110°C) |
| 7) Starch – KI paper | 14) Suction filtering apparatus with Buchner funnel. |

Procedure :

Place 7 g of sulphanilic acid dihydrate, 1.8 g of anhydrous sodium carbonate and 70 ml of water in a 250 ml beaker and warm until a clear solution sodium sulfanilate (1) is obtained. Cool the solution to 10-15°C and add slowly with stirring a solution of 2.5 g of sodium nitrite in 7 ml water. Pour the resulting mixture slowly with stirring into a mixture of 7 ml of conc. hydrochloric acid and 40 g of crushed ice contained in a 500 ml beaker. Test for the presence of free nitrous acid (with starch-potassium iodide paper) after 15 minutes. Fine crystals of sodium diazobenzene sulphonate salt (2) soon separates. Dissolve 4.2 ml of dimethylaniline (3) in 2 ml glacial acetic acid and add this mixture with vigorous stirring to the solution of sodium diazobenzene sulphonate (2). Allow the mixture to stand for 10 minutes. The red coloured acid form of methyl orange gradually separates. Now add slowly with constant stirring 25 ml of 20 per cent sodium hydroxide solution. The reaction mixture becomes orange due to separation of sodium salt of methyl orange (4). Heat the solution with stirring almost to boiling, when most of the methyl orange passes into solution. Add 7 g sodium chloride and warm at 80-90°C until the salt dissolves completely. Allow the mixture to cool undisturbed for 15 minutes and then cool in a ice-water bath. Filter of the precipitated

methyl orange at the pump. Rinse the beaker with a little saturated solution of NaCl and drain well. Recrystallise the crude product from ~ 100 ml hot water (filter the hot solution under suction if necessary through a preheated Buchner funnel). Reddish – orange crystals of methyl orange separates after cooling. Filter the crystals at the pump, drain well, wash with little ethanol and finally with little ether. The yield is ~ 8.5 g. Methyl orange, being a salt (4) has no well-defined m.p.

Experiment No. – 18 : Preparation of diazoaminobenzene



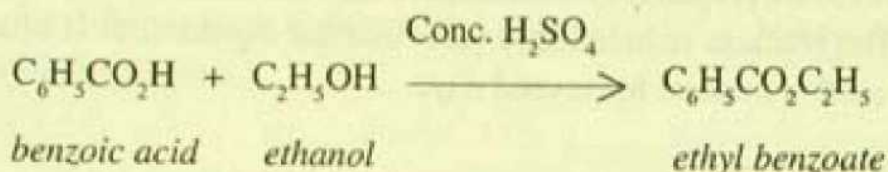
Chemicals & Apparatus required

- | | |
|----------------------------|-------------------------------------|
| 1) Aniline | 6) Ice |
| 2) Conc. hydrochloric acid | 7) Conical flask (100 ml) |
| 3) Sodium nitrite | 8) Thermometer (0° – 110°C) |
| 4) Hydrated sodium acetate | 9) Suction filtering apparatus with |
| 5) Light petrol (60°-80°) | Buchner funnel. |

Procedure :

Place 20 ml of water, 5 ml of conc. hydrochloric acid and 3.5 ml of redistilled aniline in a 100 ml conical flask. Shake the mixture thoroughly and add 13 g of crushed ice. Run in a solution of 1.3 g of sodium nitrite in 4 ml of water with constant shaking during 5 minutes. Allow the mixture to stand with occasional shaking for 10 minutes and then add a solution of 5.3 g of crystallised sodium acetate in 10 ml of water during 5 minutes. A yellow precipitate of diazoaminobenzene starts to form at once. Allow the mixture to stand with occasional shaking for half an hour, keeping the temperature below 20° (add ice if necessary). Collect the product by filtration under suction, wash with cold water (~ 50 ml), drain well and dry on a sheet of blotting paper. The yield of the crude product will be ~ 3.5 g. Recrystallise a small portion from light petrol (60°-80°) (**Caution, Inflammable**) to obtain pure diazoaminobenzene of m.p. 97°C.

Experiment No. - 19 : Preparation of ethyl benzoate



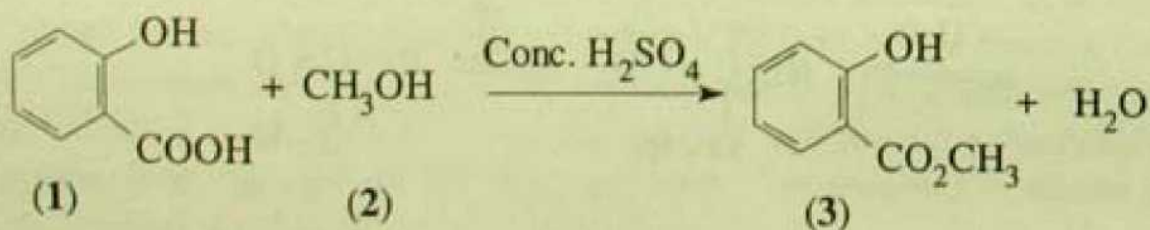
Chemicals & Apparatus required :

- | | |
|-------------------------|------------------------------|
| 1) Benzoic acid | 6) Anhydrous sodium sulphate |
| 2) Absolute ethanol | 7) 250 ml R.B. flask |
| 3) Conc. sulphuric acid | 8) Reflux condenser |
| 4) Sodium carbonate | 9) Air bath |
| 5) Ether | 10) Separatory funnel |

Procedure :

Place 10 g of benzoic acid, 35 ml of absolute alcohol (ethanol) and 1 ml of conc. sulphuric acid in a 250 ml round-bottomed flask equipped with a reflux condenser. Add a few boiling chips and boil the mixture gently on a heating mantle under reflux for 2 hours. Remove the excess ethyl alcohol by distillation from a hot water bath and pour the residue into 100 ml of cold water. Neutralise with solid sodium carbonate and extract the resulting oil with 100 ml of diethyl ether (**Caution, Inflammable**) in a separatory funnel. Separate the ethereal layer, wash it with ice cold water, dry with anhydrous sodium sulphate, filter and distil off the ether (**Caution, Inflammable**) Finally distil the residue from an air bath, collecting the ethyl benzoate as a colourless liquid of b.p. 212°-214°C. The yield is ~ 9.0 g.

Experiment No. - 20 : Preparation of methyl salicylate



Chemicals & Apparatus required :

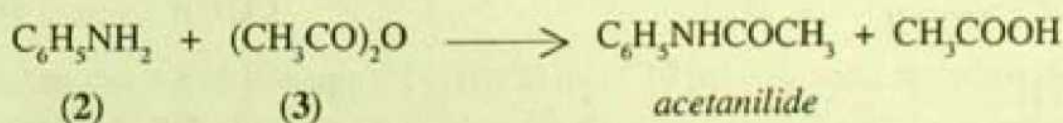
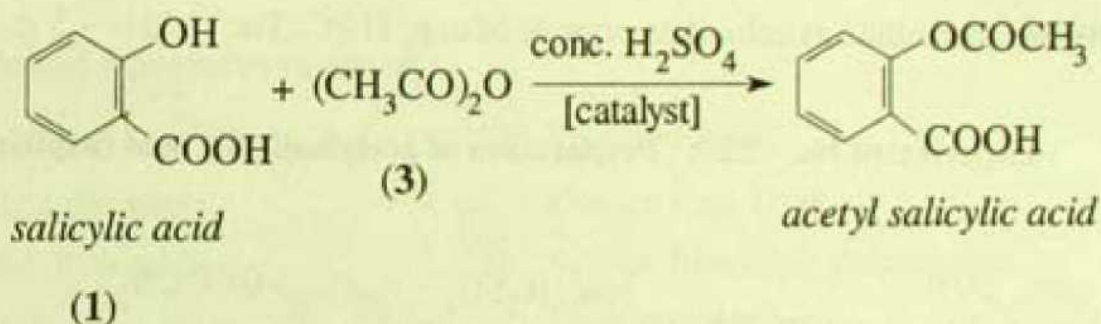
- | | |
|---------------------|------------------------------|
| 1) Salicylic acid | 6) Anhydrous sodium sulphate |
| 2) Dry methanol | 7) 250 ml R.B. flask |
| 3) Conc. H_2SO_4 | 8) Reflux condenser |
| 4) Sodium carbonate | 9) Air bath |
| 5) Ether | 10) Separatory funnel |

Procedure :

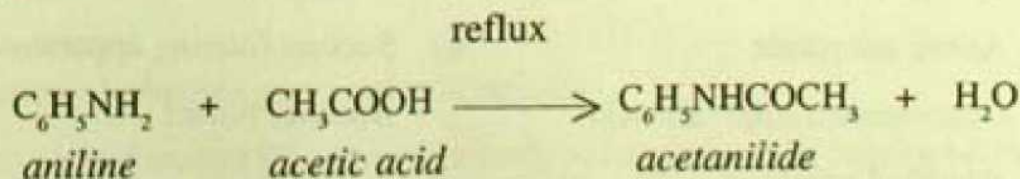
Use 14 g of salicylic acid (1), 40 ml of dry methanol (2) and 4 ml of conc. sulphuric acid. Reflux the mixture for at least 5 hours and work up as for ethyl benzoate. Collect the pure methyl salicylate (3) (a colourless oil of delightful fragrance, *oil of wintergreen*) at 221° - $224^{\circ}C$ (b.p.). The yield is ~12.5 g.

8. Acetylation of phenols and aromatic amines

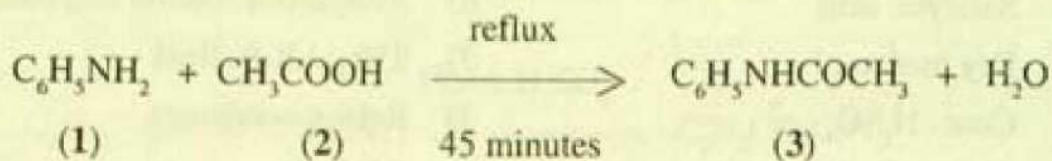
Phenols (1) and amines (2) can be conveniently acetylated with acetic anhydride (3) alone or, in the presence of catalytic amount of sulphuric acid, or, in the presence of aqueous alkali depending upon the nature of compound to be acetylated.



Acetic anhydride – pyridine and acetic anhydride-sodium acetate (anhydrous) are also very useful reagents for acetylation of phenols and amines. Glacial acetic acid may also be used for acetylation of amines, e.g.,



Experiment No. - 21 : Preparation of acetanilide



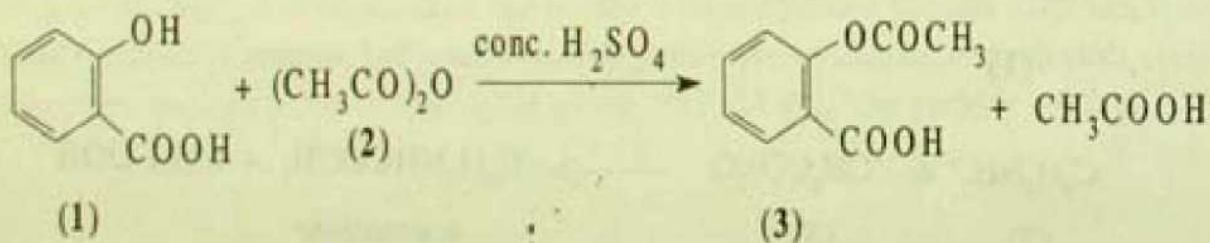
Chemicals & Apparatus required

- | | |
|------------------------|-------------------------------------|
| 1) Aniline | 5) Ice |
| 2) Glacial acetic acid | 6) Suction filtering apparatus with |
| 3) 100 ml R.B. flask | Buchner funnel |
| 4) Reflux condenser | |

Procedure :

Place 7 ml aniline (1) and 20 ml glacial acetic acid (2) in a 100 ml dry round-bottomed flask fitted with a reflux condenser. Add some boiling chips and heat the mixture under reflux for 45 minutes. Cool the reaction mixture and pour it, with stirring, into 150 g ice-water mixture taken in a beaker. Acetanilide (3) separates as shining white crystals. Filter the under suction, wash with cold water, drain well. Recrystallise from hot water to obtain pure acetanilide as colourless crystals of m.p. 114°C. The yield is ~ 5 g.

Experiment No. - 22 : Preparation of acetylsalicylic acid (aspirin)



Chemicals and Apparatus required :

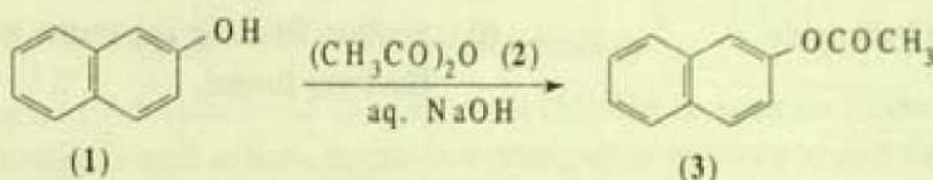
- | | |
|--------------------------------|-------------------------------------|
| 1) Salicylic acid | 5) Conical flask |
| 2) Acetic anhydride | 6) Suction filtering apparatus with |
| 3) Concentrated sulphuric acid | Buchner funnel |
| 4) Rectified spirit | |

Procedure :

Place 5 g of salicylic acid (1) and 7 ml of acetic anhydride (2) in a small conical flask, add 5 drops of concentrated sulphuric acid and swirl the flask in order to secure thorough mixing. Warm on a hot water bath at 50°-60° for 15 minutes while stirring with a glass rod. Allow the mixture to cool and stir occasionally. Add 75 ml of water, stir well. Acetylsalicylic acid (aspirin) (3) separates as shining white crystals. Filter the product under suction. Recrystallise from 50 ml of (30 : 70) ethanol-water mixture, when shining white needle-like crystals of aspirin are obtained. The yield is ~ 5.5 g.

Note : Acetylsalicylic acid decomposes when heated at (128° – 135°C) and does not possess a sharp m.p.

Experiment No. 23 : Preparation of β -naphthyl acetate



Chemicals and Apparatus required :

- | | |
|----------------------|-------------------------------------|
| 1) β -Naphthol | 5) Rectified spirit |
| 2) Acetic anhydride | 6) Conical flask (100 ml) |
| 3) Sodium hydroxide | 7) Suction filtering apparatus with |
| 4) Ice | Buchner funnel |

Procedure :

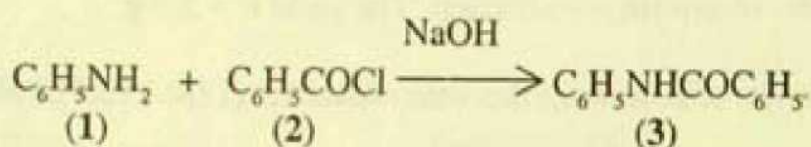
Dissolve 4 g of β -naphthol (1) in 20 ml of 10 per cent sodium hydroxide solution in a 100 ml conical flask. Add 15 g of crushed ice and then 5 ml acetic anhydride (2). Stopper the flask and shake vigorously for 30 minutes (occasionally open the stopper of the flask to release the pressure inside). Filter the resulting solid at the pump, wash with water, drain well. Recrystallise from aqueous ethanol. The yield of β -naphthyl acetate is ~5 g. and its m.p. is 71°C.

9. Benzoylation of phenols and aromatic amines

Phenols (1) and amines (2) can conveniently be benzoylated by *Schotten-Baumann method* with benzoyl chloride (3) in the presence of aqueous sodium hydroxide solution.



Experiment No. - 24 : Preparation of benzanilide



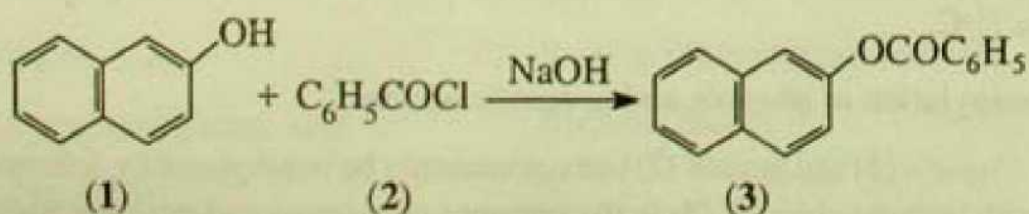
Chemicals and Apparatus required :

- | | |
|---------------------|---|
| 1) Aniline | 4) Rectified spirit |
| 2) Benzoyl chloride | 5) Conical flask (150 ml) |
| 3) Sodium hydroxide | 6) Suction filtering apparatus with Buchner funnel. |

Procedure :

Place 3 ml of aniline (1) and 30 ml of 10 per cent aqueous sodium hydroxide solution in a 150 ml conical flask and add 4.5 ml of benzoyl chloride (2), stopper the flask and shake vigorously for 10-15 minutes while opening the stopper occasionally to release the pressure inside the flask. The crude benzanilide (3) separates as white solid. When the reaction is complete (i.e. when no odour of benzoyl chloride is perceived (**Caution Eye Irritating**)) make sure that the reaction mixture is alkaline. Filter the product under suction, wash with water and drain well. Recrystallise the crude product from hot rectified spirit (filter the hot solution under suction through a preheated Buchner funnel, if necessary). Collect the colourless crystals of benzanilide and dry in air. The yield of benzanilide is ~ 5.5 g. and its m.p. is 162°C.

Experiment No. - 25 : Preparation of 2-naphthyl benzoate



Chemicals and Apparatus required

- | | |
|---------------------|-------------------------------------|
| 1) 2-Naphthol | 5) Conical flask (150 ml) |
| 2) Benzoyl chloride | 6) Suction filtering apparatus with |
| 3) Sodium hydroxide | Buchner funnel |
| 4) Rectified spirit | |

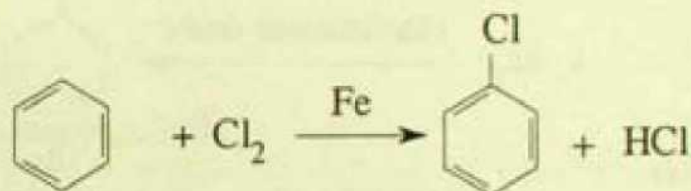
Procedure :

Dissolve 5 g. of 2-naphthol (1) in 35 ml of 5 per cent sodium hydroxide solution in the cold in a 150 ml conical flask and add 4.5 ml of benzoyl chloride (2). Stopper the flask and shake vigorously until the odour of benzoyl chloride disappears (10-15 minutes). 2-Naphthyl benzoate (3) separates as a solid product. Collect the solid by filtration under suction and wash with cold water till free from alkali.

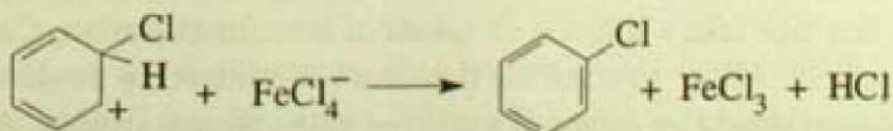
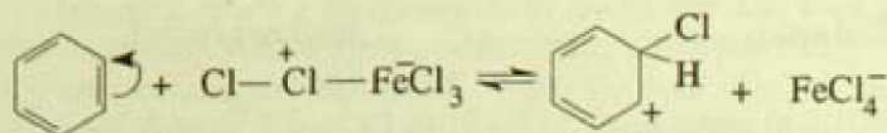
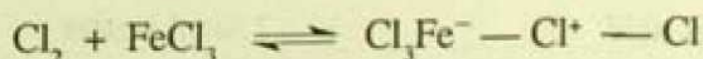
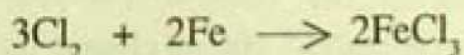
Recrystallise crude product from about 40 ml of rectified spirit. Collect the crystals by filtration under suction, drain well and dry upon filter paper in the air. The yield of pure 2-naphthyl benzoate is ~ 7.5 g. and its m.p. is 110°C.

10. Halogenation

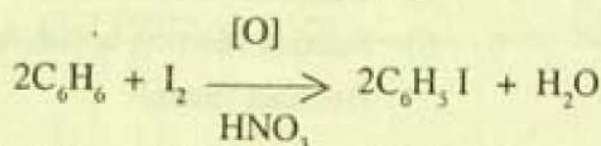
Nuclear substitution of benzene with chlorine or bromine occurs readily in the presence of catalysts such as iron, aluminium amalgam or pyridine to give monohalogenated derivatives as the main product.



Disubstituted products (mainly the *para*-isomers) are obtained if the proportion of halogen is increased. Mechanism of halogenation of benzene involves the following steps :

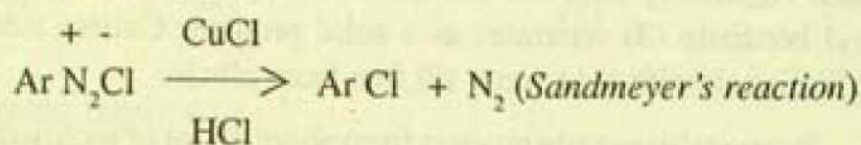


Iodine is least active of the halogens and direct iodination does not occur unless the reaction is carried out in the presence of an oxidising agent such as fuming nitric acid :

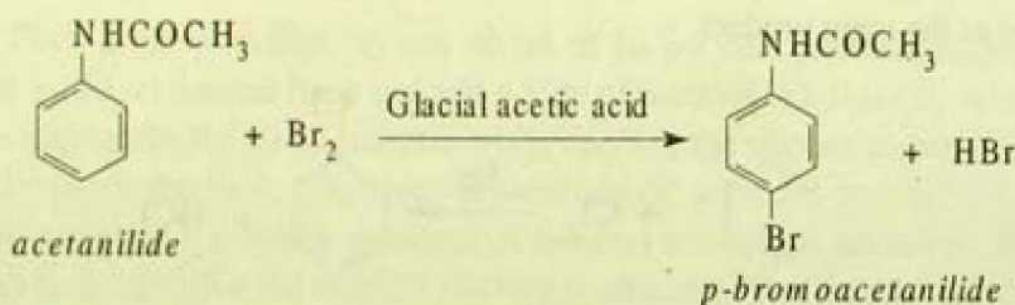


The groups $-\text{NH}_2$, $-\text{OH}$ or $-\text{NHCOCH}_3$ activates the aromatic ring towards electrophilic attack by chlorine or bromine.

Aromatic halogen derivatives can also be prepared through aromatic diazo compounds with suitable halides :



Example No. - 26 : Preparation of *p*-bromoacetanilide



Chemical and Apparatus :

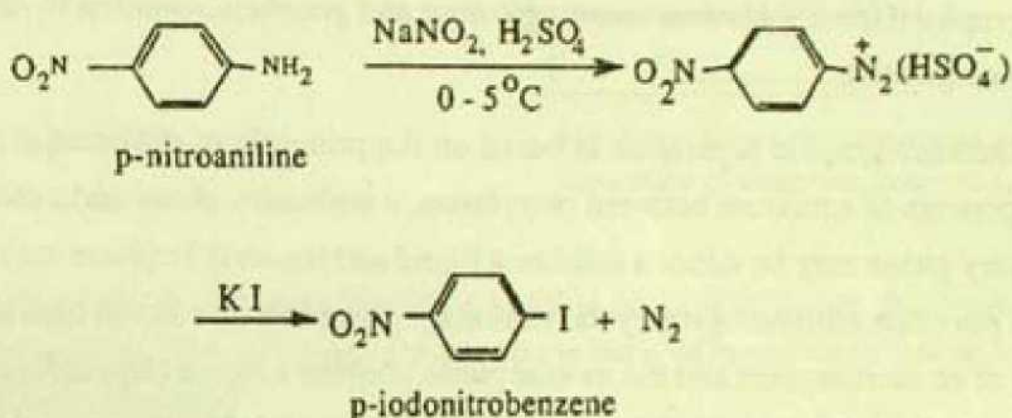
- | | |
|--------------------------|-------------------------------------|
| 1) Acetanilide | 6) Test tube, dropper |
| 2) Bromine | 7) 100 ml conical flask |
| 3) Glacial acetic acid | 8) 250 ml beaker |
| 4) Sodium metabisulphite | 9) Suction filtering apparatus with |
| 5) Rectified spirit | Buchner funnel |

Procedure :

Dissolve 3.4 g of acetanilide in 12 ml of glacial acetic acid in a 100 ml conical flask. In a test tube take a solution of 1.4 ml of bromine (**Caution, Corrosive**) in 7 ml of glacial acetic acid. Allow to stand the flask with its contents in a cold water bath. Add the bromine solution slowly by means of a dropper with constant shaking. After the addition of

bromine is complete the solution will have an orange colour due to slight excess of bromine (a part of the product may crystallise out). Allow the reaction mixture to stand for 30 minutes at room temperature with occasional shaking. Pour the reaction mixture into 100 ml of water taken in a 250 ml beaker, rinse the flask with about 25 ml of water. Add 5% sodium metabisulphite solution drop by drop just to remove the yellow colour of the solution due to unreacted bromine. Filter the resulting crystalline precipitate of *p*-bromoacetanilide under suction, wash thoroughly with cold water and drain well. Recrystallise the product from aqueous ethanol (rectified spirit). *p*-Bromoacetanilide appears as colourless crystals of m.p. 167°C. The yield is ~ 4.5 g.

Example No. - 27 : Preparation of *p*-iodonitrobenzene



Chemicals and Apparatus required :

- | | |
|--------------------------------|-------------------------------------|
| 1) <i>p</i> -Nitroaniline | 6) Ethanol |
| 2) Sodium nitrite | 7) 100 ml beaker (two) |
| 3) Concentrated sulphuric acid | 8) Thermometer |
| 4) Potassium iodide | 9) Suction filtering apparatus with |
| 5) Ice salt bath | Buchner funnel. |

Procedure :

Place 2 g of *p*-nitroaniline, 12 ml of water and 1.7 ml conc. sulphuric acid in a 100 ml beaker. Stir for 20 minutes. Place a thermometer in the beaker and cool the reaction mixture to 0° – 5°C (ice-salt bath). Add dropwise with stirring a solution of 1 g of NaNO₂ in 3 ml of water keeping the temperature below 5°C. Filter the cold solution and add the filtrate with stirring to a solution of 4 g of KI in 12 ml of water taken in a 100 ml beaker. Collect the precipitated solid by filtration under suction and then shake it with sodium thiosulphate solution to remove the excess of iodine. Filter off the product, wash with water, drain well and dry by suction, then recrystallise from ethanol. The yield of *p*-iodonitrobenzene is ~2.5 g. Its m.p. is 171°-173°C.



Chapter – 8

Chromatographic Separations

Introduction

Chromatography is a widely used analytical technique for separation, isolation, purification and identification of organic, inorganic and biochemical compounds from complex mixtures. Russian botanist Mikhail Tswett first employed the technique in 1906 to separate various plant pigments such as chlorophylls, carotenes and xanthophylls by passing the plant extracts through glass column packed with finely divided calcium carbonate. The separated species appeared as coloured bands on the column from which the name *Chromatography* (Greek – *khroma* meaning colour and *graphein* meaning to draw a graph or to write) originated.

Chromatographic separation is based on the principle of differential distribution of the components of a mixture between two phases, a stationary phase and a mobile phase. The stationary phase may be either a solid or a liquid and the mobile phase may be a liquid or a gas. In *partition chromatography* the stationary phase is a thin liquid film adsorbed on the surface of an inert support and the mobile phase is either a liquid (*liquid-liquid partition chromatography*) or a gas (*gas-liquid partition chromatography*). In either case, the separation depends largely upon the partition of the components present in the mixture between two phases. *Paper chromatography* is an example of partition chromatography. In *adsorption chromatography*, the stationary phase is a finely divided solid adsorbent such as alumina, silica gel etc. and the mobile phase is usually a liquid (*solid-liquid chromatography*). Here the separation depends upon the selective adsorption of the components of the mixture on the surface of the solid.

Paper chromatography :

Paper chromatography is a form of partition chromatography in which the stationary phase is absorbed water molecules present in the filter paper (ca 22%) supported by the cellulose molecules of the paper. A paper strip made from Whatman No. 1 filter paper is spotted at one end with the solution of the test sample to be investigated by means of a capillary tube and dried in air. The paper is then supported vertically in a closed jar containing the developing solvent which is the mobile phase in such a way that the paper edge nearest

to the spot origin just dips into the solvent (*ascending technique*). The solvent level is kept well below the spot [Fig. 1a]. Development of the chromatogram occurs by upward movement of the solvent by capillary action.

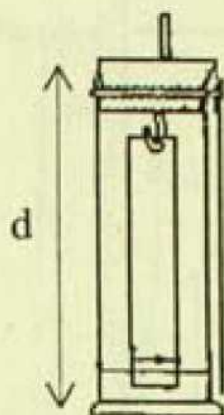


Fig. 1(a) Paper chromatography

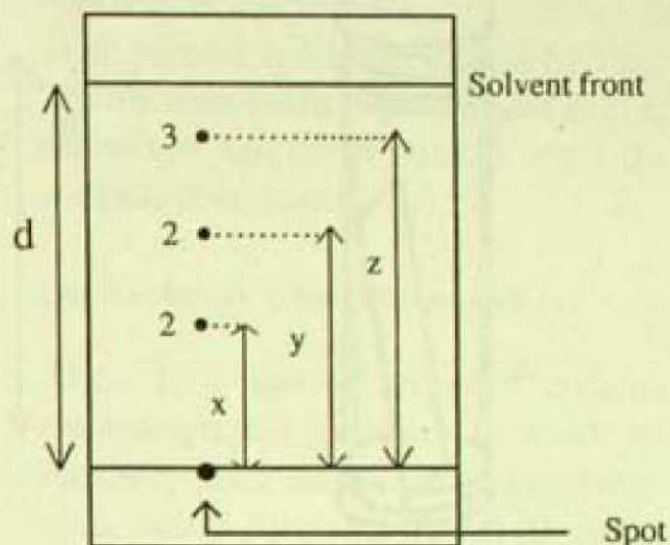


Fig. 1(b) : Paper chromatogram :
Separation of three components 1, 2 and 3.

The paper is then dried and sprayed with a suitable reagent to locate the position of the separated components. Identification is made on the basis of *retention factor* or *retardation factor* (R_f values) defined as :

$$R_f = \frac{\text{distance moved by the solute}}{\text{distance moved by the solvent front}}$$

Fig. 1(b) indicates the method of measurement of R_f values of each of the components of a typical chromatogram. R_f values of compounds 1, 2 and 3 are x/d , y/d and z/d respectively, where, D is the distance moved by the solvent front and x , y and z are the distances moved by the compounds 1, 2 and 3 respectively.

Thin layer chromatography :

Thin layer chromatography is a special case of adsorption chromatography where the stationary phase is a thin uniform layer of adsorbent (silica gel, alumina etc.) coated on a glass strip with the help of a binding agent which is incorporated. The chromatoplate so prepared is spotted near one edge with a minute volume of the solution containing the components to be separated and then placed vertically in contact with a suitable solvent (the mobile phase) taken in a closed cylindrical glass jar, keeping the solvent level well below the spots [Fig. 2(a)]. Development of the chromatogram occurs by upward movement of the

solvent front by capillary action. The plate is then dried and sprayed with a suitable reagent to locate the positions of the separated components..



Fig. 2(a). Thin layer chromatography

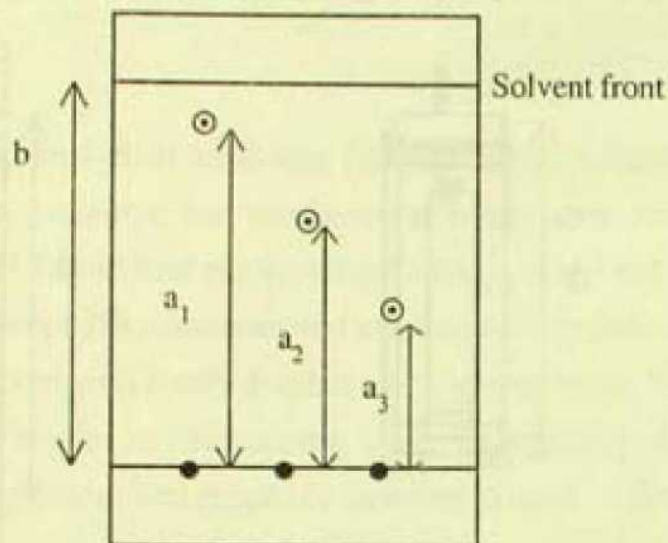


Fig. 2(b). Thin layer chromatogram.

Identification of components may be done from their R_f values Fig. 2(b). If b is the distance moved by the solvent front and a_1 , a_2 and a_3 the distances moved by the components 1, 2, and 3, then their R_f values will be given by :

$$R_{f_1} = \frac{a_1}{b}, R_{f_2} = \frac{a_2}{b}, \text{ and } R_{f_3} = \frac{a_3}{b} \text{ respectively.}$$

Column chromatography :

Column chromatography is carried out in cylindrical glass tubes, usually narrower at the bottom end with a stopcock (Fig. 3). The length (range ~ 10 – 90 cm) and diameter (range ~ 1 – 5 cm) of the column tube depend on the amount of the substance to be adsorbed or separated. The tube is clamped vertically and filled with a suitable adsorbent (alumina or silica gel etc.) which serves the stationary phase. The sample (mixture of components), dissolved in minimum volume of a suitable solvent is then introduced at the top of the column. The column is then eluted with a series of suitable solvents (the mobile phase), beginning with the least polar one. The chromatogram is developed by gravity flow of solvents. Compound which is less strongly adsorbed, will be washed down the column of adsorbent at a faster rate than the one which is more strongly adsorbed and this is how they are separated on the column. When the components under investigation are coloured, different coloured zones, or, bands are developed on the chromatogram. These bands are then separated

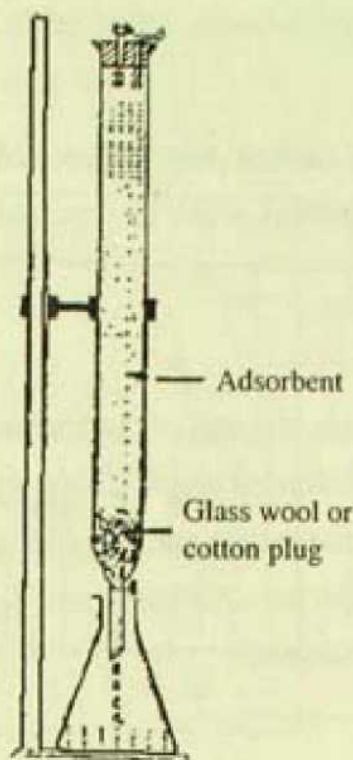


Fig. 3. Column Chromatography

by elution with suitable solvents and the individual components are then recovered. When the compounds are colourless, fractions of the effluent are collected in small portions and are monitored by TLC. The fractions which give same spot in TLC are mixed and concentrated, when the component crystallises out.

Ion Exchange Chromatography :

This is a special type of column chromatographic separation in which the stationary phase may be a cation exchange resin, such as Amberlite IR-120 (H^+ form), Dowx - 50, Duolite C225 (Na^+ form), or an anion exchange resin Amberlite IR-400 (OH^- form), Dowex -1, Duolite A113 (Cl^- form) etc. This technique is suitable for separation of ionic components.

(a) Experiments based on paper chromatography

Experiment No. 1 : Separation and identification of amino acids in a mixture (*DL*-alanine, *L*-lysine and *L*-leucine) by paper chromatography :

Materials and Apparatus required :

- | | |
|---|---|
| 1. Amino acids (<i>DL</i> -alanine, <i>L</i> -lysine, <i>L</i> -leucine) | 7. 1-Butanol |
| 2. Acetic acid | 8. Sprayer |
| 3. Measuring cylinders (25 ml, 10 ml) | 9. Distilled water |
| 4. Test tubes | 10. Fine capillary tubes |
| 5. Electrical air oven (100° - $110^\circ C$) | 11. Whatman No.1 chromatography paper strip (20 cm x 4 cm) |
| 6. Solvent chamber (development jar) (20 cm x 4 cm) | 12. Spraying reagent : 0.3% ninhydrin solution in 95% ethanol |

Procedure :

(a) Preparation of the sample solutions :

Prepare the solutions by dissolving 10-15 mg of each of pure samples of the amino acids and of the given unknown mixture in ~ 1 ml of distilled water in separate test tubes and label them accordingly.

(b) Application of the sample :

Draw with a pencil a base line (~3 cm) above the lower end of the chromatography paper strip. Put four pencil dots on the base line at equal distances apart. Using separate fine capillary tubes put spots of the solutions of three known amino acids and that of the unknown mixture on the pencil dots (diameters of the spots should be ~2-3 mm) and record their respective positions. Allow the spots to dry in air for 5 minutes.

(c) Preparation of the developing solvents :

Prepare the required quantity of the developing solvent by mixing 1-butanol, acetic acid and distilled water respectively in 12 : 3 : 5 (v/v/v) proportion. Pour the solvent into the developing jar, cover the same with the lid, swirl the solvent inside and allow to stand for a few minutes.

(d) Development of the chromatogram :

Open the jar and suspend the paper strip into the developing solvent to a depth of ~ 1 cm keeping the solvent level well below the base line [Fig. 1(a)]. Care must be taken so that the paper strip does not touch the side of the vessel. Allow the solvent to ascend upto ~ 14-15 cm from the base line (it will take about 2 hours). Then remove the paper strip from the jar, mark the solvent front with a pencil and dry the paper in air.

(e) Location of the spots :

Spray the ninhydrin reagent on both side of the dried paper chromatogram and then dry the paper at 100°-110° by suspending vertically in an electrical air oven (or dry the paper with a warm-air blower) for ~ 5 minutes, when blue or purple colours are visible at the respective positions of the amino acids on the chromatogram. Encircle the developed spots with pencil marks and measure the distances moved by the amino acids and the also distance moved by the solvent front from the base line. Calculate the R_f values and identify

the amino acids in the unknown mixture by comparison of their R_f values with those of the standards (Fig. 4).

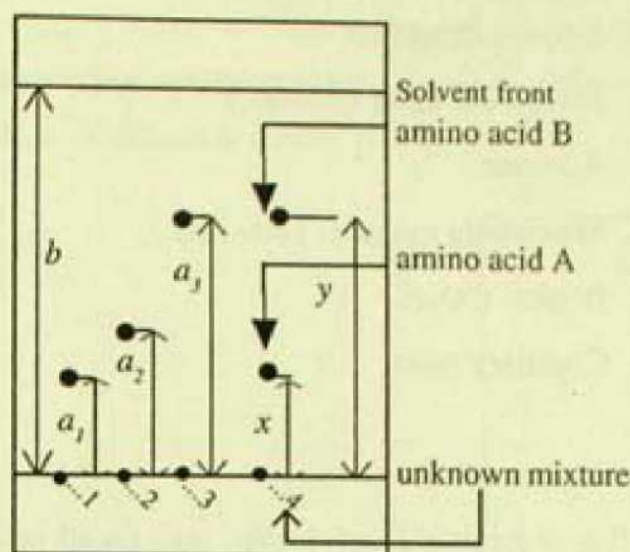


Fig.4 : Paper chromatogram :
1, *L*-lysine; 2, *DL*- alanine
3, *L*-leucine; 4, unknown

Experimental results

Evaluation of R_f values :

R_f (<i>L</i> -lysine)	R_f (<i>DL</i> -alanine)	R_f (<i>L</i> -leucine)	Unknown mixture	
			R_f (A)	R_f (B)
$\frac{a_1}{b} = \dots$	$\frac{a_2}{b} = \dots$	$\frac{a_3}{b} = \dots$	$\frac{x}{b} = \dots$	$\frac{y}{b} = \dots$

From comparison of R_f values of the components A and B (in the unknown mixture) with those of the standards (1, 2 and 3) the amino acids A and B may identified to be *L*-lysine and *L*-leucine respectively.

Approximate R_f values of the amins acids :

L-leucine (0.62)

L-lysine (0.17)

DL-alanine (0.35)

Experiment No. 2 : Separation of leaf pigments of spinach leaves by paper chromatography

Green spinach leaves contains a number of natural pigments including chlorophylls (the green pigments of plant), carotenes (yellow pigments, like those found in carrots, which are precursor to vitamin A) and xanthophylls (which also have a yellow colour and may be

regarded as partially oxidised carotenes). These pigments may be separated as respective colour bands by paper chromatographic experiments.

Materials and Apparatus required :

- | | |
|--|---------------------------------|
| 1. Fresh spinach leaves (~10 g) | 7. Solvent chamber |
| 2. Mortar and pestle | 8. Petroleum ether (60°-80°) |
| 3. Funnel | 9. Acetone |
| 4. Cotton | 10. Measuring cylinder (100 ml) |
| 5. Anhydrous sodium sulphate | 11. Beaker (50 ml) |
| 6. Whatman No. 1 chromatography paper strip (20 cm x 3 cm) | 12. Capillary tube |

Procedure :

- Extraction of spinach leaves : Tear ~10 g of fresh spinach leaves into small pieces and place them in a mortar. Add 20 ml of petroleum ether-acetone (80 : 20 v/v) mixture and grind the spinach leaves with a pestle until the liquid is dark green. Dry the deep green liquid by treating it with a small amount of anhydrous sodium sulphate taken in a 100 ml dry conical flask. Decant the green liquid into another small dry conical flask. Wash the sodium sulphate with 2-5 ml of petroleum ether and preserve the combined extract and the washings for chromatographic separation.
- Draw a pencil line about 3 cm from the bottom of the paper strip. Put a spot of the deep green extract on the pencil line using a fine capillary tube. The spot should not be wider than 3 mm diameter. Let the spot dry and then put another spot of the extract on the first one and dry as before. Repeat the sequence until the pigment spot on the paper is deep green coloured (as many as 10-15 spotting may be required).
- Prepare the developing solvent by mixing 95 ml of petroleum ether and 5 ml of acetone. Pour the solvent into the developing jar so that the height of the solvent level is 1.5 cm to 2 cm. Cover the jar with its lid and swirl the solvent inside the jar and allow to stand for a few minutes.
- Open the jar and suspend the paper strip into the developing solvent to a depth of ~1 cm keeping the solvent level well below the base line (Fig. 1a). Let the chromatogram develop without disturbance until the solvent ascend upto ~ 15 cm from the base line. Take the paper strip out of the jar and immediately mark the location of the solvent front with a pencil line, and allow the paper strip to dry in air. Drying should be carried out in subdued light since the pigments are gradually destroyed on exposure to sunlight or to fluorescent light, which causes the colour to fade.

Experimental results :

Four coloured spots are separated in the chromatogram (Fig. 5) : a yellow band almost with the solvent front (carotene pigments), then several bands near the middle in the descending order – yellow ($R_f \sim 0.75$, xanthophyll pigments), grass green ($R_f \sim 0.66$, chlorophyll-a) and olive green ($R_f \sim 0.57$, chlorophyll-b). The diagram shows the approximate location of different colour bands.

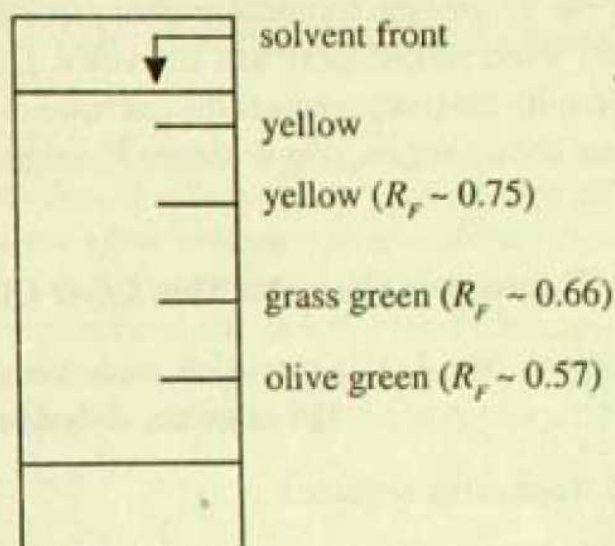


Fig. 5 : Chromatogram of the spinach leaf extract

Experiment No. 3 : Separation and identification of sugars (glucose fructose and sucrose) by paper chromatography.

Materials and Apparatus required :

- | | |
|--|---------------------|
| 1. Sugars (glucose, fructose and sucrose) | 6. Test tubes |
| 2. Whatman No. 1 chromatography paper strip (20 cm x 4 cm) | 7. Distilled water |
| 3. Fine capillary tubes | 8. 1-Butanol |
| 4. Measuring cylinders (25 ml, 10 ml) | 9. Acetic acid |
| 5. Spraying reagent : | 10. Solvent chamber |
| | 11. Sprayer |

Aniline oxalate : Dissolve 0.093 g (~ 9-10 drops of aniline) in 50 ml of 95% ethanol and mix with 50 ml of 0.2 (M) aq. oxalic acid.

Procedure :

Set up the apparatus as discussed in the experiment No. 1. Prepare the developing solvent by mixing 1-butanol, acetic acid and water in the ratio 4 : 1 : 5 (v/v/v) respectively. Prepare the solutions of glucose, fructose and sucrose by dissolving ~ 30 mg of each sugar in ~0.25 ml of water in separate test tubes. Using fine capillary tubes, put spots of the three sugar solutions and of the unknown solution separately on the paper strip and dry the same in air. Develop the chromatogram using the developing solvent mentioned above (as described in experiment No. 1). Dry the chromatographic paper and spray the same with the aniline oxalate reagent, when yellow spots will be visible. Determine the R_f values of the pure components. Identify the components of the unknown mixture by comparing their R_f values with those of the known sugars. (Approximate R_f values : sucrose : (0.08), glucose : (0.17) and fructose : (0.25).

(b) Experiments based on Thin Layer Chromatography (TLC)

Experiment No. 4 : Separation and identification of amino acids (*DL*-alanine, *L*-lysine and *L*-leucine) by TLC.

Materials and Apparatus required :

- | | |
|---|---|
| 1. Amino acids (<i>DL</i> -alanine, <i>L</i> -lysine, <i>L</i> -leucine) | 8. 1-Butanol |
| 2. Silica gel G for TLC | 9. Acetic acid |
| 3. Chloroform | 10. Distilled water |
| 4. Glass plates (12 cm x 4 cm) | 11. Solvent chamber |
| 5. Fine capillary tubes | 12. Air oven (100°-110°C) |
| 6. Sprayer | 13. Spraying reagent : 0.3% ninhydrin in 95% ethanol solution |
| 7. Tongs | |

Procedure

(a) Preparation of the chromatoplate

Make a slurry of 33 g of silica gel in 100 ml of chloroform in a wide-mouth stoppered bottle. Shake well and dip a glass plate nearly horizontally, with the help of a pair of tongs into the homogeneous slurry. Take the plate out and place it horizontally on a rack, dry in air for 10 minutes. Scrap off the silica gel from the bottom side of the plate.

(b) Preparation of the developing solvent

Prepare the developing solvent by mixing 80 ml of 1-butanol, 20 ml of acetic acid and 20 ml of distilled water in a bottle.

(c) Preparation of the sample solution

Prepare the solutions of the pure amino acids and the unknown mixture sample by dissolving 10-15 mg each of the substance in 1 ml of distilled water separately in four test tubes and label them accordingly.

(d) Application of the sample

Spot the chromatoplate with the three amino acids and the unknown mixture using separate capillary tubes. The spots should be approximately ~ 1 cm above the lower edge of the plate. Diameter of the spots should not be wider than 2 mm. Dry the plate with the spots in air till the spots are no longer visible.

(e) Development of the chromatogram

Pour ~ 10 –15 ml of the developing solvent into a glass jar, cover it with the lid, swirl it thoroughly and allow to stand for a few minutes to saturate the air inside the jar with solvent vapour. Open the jar and insert the spotted chromatoplate carefully inside it by means of a pair of tongs keeping the spotted end downward, so that the solvent touches the adsorbent layer well below the spots. Cover the jar with the lid and allow the solvent to rise about 10 cm. Remove the plate, place it on a rack and allow to dry in air for ~ 10 to 15 minutes.

(f) Location of the spots

Spray the dried plate with ninhydrin reagent and heat the plate at 100°-110°C for 5-10 minutes in an air oven in order to develop the colours (blue or purple colour are produced when amino acids react ninhydrin reagent). Mark the centre of each spot with a metal scribe and evaluate the respective R_f values. Identify the amino acids present in the unknown mixture by comparing the R_f values of the components of the mixture with those of the standards. Draw a sketch of the chromatogram showing the parameters you have measured (Fig. 6).

Experimental results

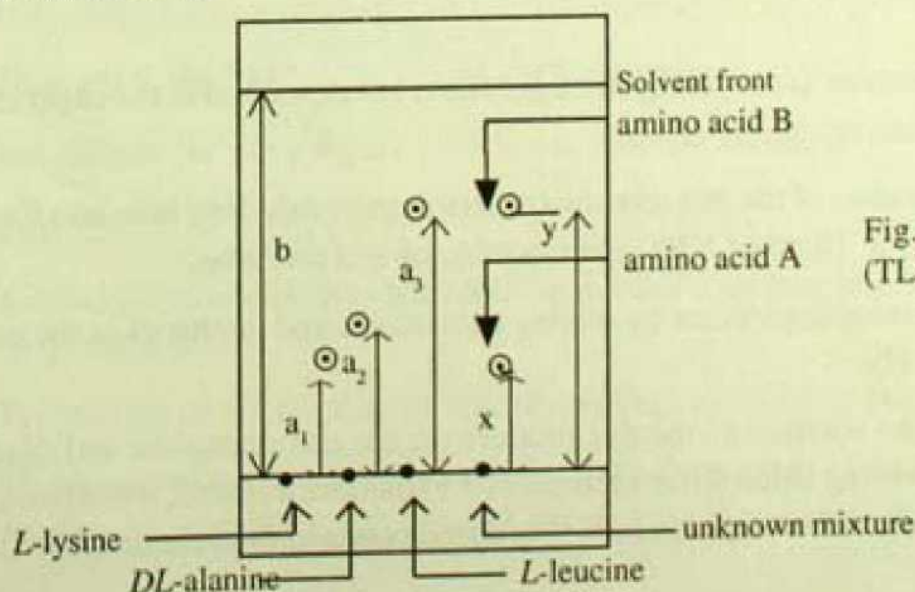


Fig. 6 : Sketch of the (TLC) chromatogram

Evaluation of R_f values :

R_f (L-lysine)	R_f (DL-alanine)	R_f (L-leucine)	Unknown mixture	
			R_f (A)	R_f (B)
$\frac{a_1}{b} = \dots$	$\frac{a_2}{b} = \dots$	$\frac{a_3}{b} = \dots$	$\frac{x}{b} = \dots$	$\frac{y}{b} = \dots$

Comparing the R_f values of the components of A and B of the unknown mixture with those of the standards it appears from Fig. 6 that A and B are L-lysine and L-leucine respectively.

R_f values of some amino acids :

L-lysine (0.14), DL-alanine (0.36), L-leucine (0.65).

Experiment No. 5 : Separation of mixture of dyes (fluorescein and methylene blue) by TLC.

Materials and Apparatus required :

1. Methylene blue
2. Fluorescein
3. Silica gel G for TLC
4. Chloroform
5. Glass plates (12 cm x 4 cm)
6. Solvent chamber
7. Fine capillary tubes
8. Methanol
9. Ethanol

Procedure :

- (a) Prepare the chromatoplate (using silica gel slurry) as described in the experiment No. 4 (TLC of amino acids)
- (b) Prepare the solution of the dye mixture by dissolving methylene blue and fluorescein (~ 10 mg each) in 10 ml of 50% aqueous ethanol in a test tube.
- (c) Prepare the developing solvent by mixing chloroform and methanol in the ratio (9:1) (v/v) respectively.
- (d) Put a spot of the solution of the dye mixture on the chromatoplate and develop the chromatogram using chloroform-methanol (9:1) mixture as usual, when two coloured spots will separate. The upper yellow spot corresponds to fluorescein ($R_f \sim 0.56$) and

the lower blue spot corresponds of methylene blue ($R_f \sim 0.16$) (Fig. 7). Determine the R_f values as usual

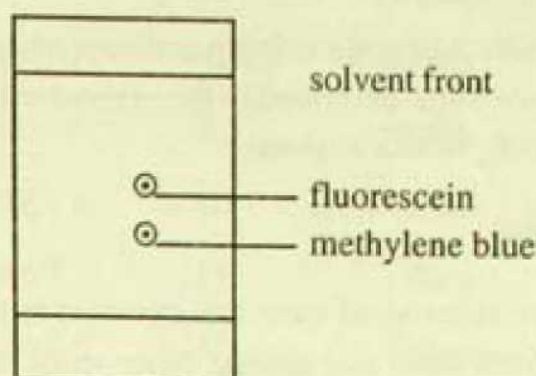


Fig. 7 : TLC separation of fluorescein and methylene blue

Experiment No. 6 : Separation of pigments from the extract of spinach leaves by TLC.

Method – 1 :

Materials and Apparatus required :

- | | |
|----------------------------------|-------------------------------|
| 1. Fresh spinach leaves (~ 10 g) | 8. Chloroform |
| 2. Mortar and pestle | 9. Measuring cylinder |
| 3. Funnel | 10. Beaker (50 ml) |
| 4. Cotton | 11. Capillary tube |
| 5. Anhydrous sodium sulphate | 12. Petroleum ether (60°-80°) |
| 6. Silica gel G for TLC | 13. Acetone |
| 7. Glass plates (12 cm x 4 cm) | 14. Solvent chamber |

Procedure :

- Extract the spinach leaves with petroleum ether – acetone (80:20) mixture as described in the experiment No. 2.
- Prepare the chromatoplate as described in the experiment No. 4.
- Using a fine capillary tube put a spot of the deep green extract of the spinach leaves on the chromatoplate. Let the spot dry and again put another spot on the top of the

first and dry as before. Repeat the sequence for several times as before (cf. Experiment No. 2).

- (d) Develop the chromatogram using petroleum ether – acetone (80:20) mixture as the developing solvent (as described in the experiment No. 4) and dry the chromatogram. Determine the R_f values as usual.

Experimental results

Several coloured spots are separated in the chromatogram : a yellow band almost with the solvent front and several other spots near the middle in the descending order : a gray spot ($R_f \sim 0.6$), a yellow spot ($R_f \sim 0.53$), two green spots ($R_f \sim 0.49$ and $R_f \sim 0.45$) and a greenish yellow spot ($R_f \sim 0.4$).

Method 2 :

Procedure :

- (a) Cut the green spinach leaves (~ 10 g) into small pieces and place them in a 250 ml beaker. Add 20 ml of 50% methanol, shake for sometime, decant off the methanol (practically containing no pigment). Place the washed leaves in a mortar, add 20 ml of petroleum ether-acetone (80 : 20) mixture and grind the leaves with a pestle, when a deep green liquid is formed. Decant the deep green liquid into a 100 ml dry conical flask, dry the extract by shaking with anhydrous sodium sulphate (4-5 g). decant the green liquid in to another small dry conical flask and wash the sodium sulphate with 4-5 ml of petroleum ether. Preserve the combined extract and the washings for TLC experiment.
- (b) Prepare the chromatoplate as described in the experiment No. 4.
- (c) Put a spot of the green extract on the chromatoplate as in method – 1 using a fine capillary tube.
- (d) Develop the chromatogram using isooctane-acetone-carbon tetrachloride (60 : 20 : 20 v/v/v) mixture as the developing solvent and dry the chromatogram in air as usual.

Experimental results :

Twelve coloured spots are separated in the chromatogram. The sequence of these spots in the descending order and their identifications are as follows :

Spot No.	Colour	Identification	Spot No.	Colour	Identification
1.	Yellow	Carotenes	7.	Green	chlorophyll- <i>b</i>
2.	Dark gray	Pheophytin <i>a</i>	8.	Yellow	Xanthophyll
3.	Light gray	Pheophytin <i>b</i>	9.	Yellow	Xanthophyll
4.	Blue	Chlorophyll <i>a'</i>	10.	Yellow	Xanthophyll
5.	Blue	Chlorophyll <i>a</i>	11.	Yellow	Xanthophyll
6.	Green	Chlorophyll <i>b'</i>	12.	Yellow	Xanthophyll

Reference: M.H. Anwar, *Journal of Chemical Education*, 1963, **40**, 29.

(c) Experiments based on column chromatography

Experiment No. 7 : Separation of pigments from the extract of spinach leaves by column chromatography

Materials and Apparatus required :

- | | |
|---|--|
| 1. Fresh spinach leaves (20 g) | 7. Measuring cylinder (100 ml) |
| 2. Mortar and pestle | 8. Petroleum ether |
| 3. Funnel | 9. Acetone |
| 4. 50 ml beaker | 10. Silica gel for column chromatography |
| 5. chromatography column (~1-1.5 cm diameter and ~40 cm long) | 11. Dropper |
| 6. Stand and clamp | 12. Conical flasks 100 ml |
| | 13. Long piece of glass rod |

Procedure :

- Extract the coloured pigments from 20 g of fresh spinach leaves with 20 ml of 80:20 mixture of petroleum ether-acetone as described in the paper chromatography experiment (Experiment No. 2).
- Mount the glass chromatography column (a 50 ml burette may be used) to a stand using a clamp. Place a small wisp of cotton or glass wool at the bottom of the column using a long piece of glass rod. On the top of the column add silica gel to fill up 15-20 cm of the column.

- c) Place a 100 ml conical flask under the column and slowly add some petroleum ether at the top of the column. After the liquid reaches the bottom, the column should drip at about 1 drop per second.
- d) Allow the chromatographic column to drip petroleum ether until the solvent level drops to just above the upper silica gel layer. Then quickly and carefully add the dark green spinach extract into the column.
- e) Allow to drip until the spinach extract level drops to just above the upper layer of the silica gel. Slowly and continually add petroleum ether so that the level of the solvent always remains above the upper silica gel level.
- f) Continue the step-(e). Two coloured bands will begin to separate from the original green spinach mixture. When the lower yellow band reaches the bottom of the column, collect this fraction in a 100 ml conical flask.
- g) After the yellow band has been collected, allow the petroleum ether level to drop below the upper silica gel layer, and start adding acetone instead of petroleum ether, keeping the solvent level always above the upper silica gel layer as before. On eluting with acetone, the green coloured band will begin to move down the column. When it reaches the bottom, collect it in another 100 ml conical flask.
- h) The pigments may be obtained in the solid state on careful evaporation of the solvents.

Experiment No. 8 : Separation of mixture of dyes (fluorescein and methylene blue) by column chromatography

Materials and Apparatus required :

- | | |
|--|-------------------------------|
| 1. Alumina (for column chromatography) | 5. Stand and Clamp |
| 2. Methylene blue | 6. Ethanol |
| 3. Fluorescein | 7. Cotton |
| 4. Glass chromatographic column
(1 cm – 1.5 cm diameter and 30 cm long) | 8. Dropper |
| | 9. Conical flasks (100 ml) –3 |

Procedure :

- a) Prepare the solution of the dye mixture as described in the experiment No. 5. Use 2 ml of this solution for column chromatographic separation.
- b) Mount the glass chromatography column (a 50 ml burette may be used) to a stand using a clamp. Place a small wisp of cotton or glass wool at the bottom of the column using a long piece of glass rod.

- c) Add alumina on the top of the column to fill up about 15 cm of this column. Keep the stopper open.
- d) Now add the solution of the dye-mixture (~2 ml) on the top of the column evenly with the help of a dropper and allow the solution to run down the column completely.
- e) Elute with 5 ml of ethanol and allow the eluant to run down the column. When the ethanol level is ~ 2-3 mm above the top of the column, add more ethyl alcohol to develop the coloured bands.
- f) Blue band of methylene blue begins to separate and moves down the column while fluorescein remains at the top. Continue addition of ethanol till the blue band reached the bottom of the column. Collect this fraction in a 100 ml conical flask until the lower end becomes colourless.
- g) Elute the column with water, when the yellow band of fluorescein immediately moves down. Continue elution with water till the yellow band reaches near the bottoms of the column. Collect this fraction in another 100 ml conical flask until the effluents appear colourless.
- h) The dyes may be obtained in the solid state on careful evaporation of the extracts.

Note : If salica gel (60-120 mesh) is used as the stationary phase instead of alumina, the sequence of coloured bands is just reversed, i.e., fluorescein begins to come out of the column first with ethanol as eluant while methylene blue remains at the top. Methylene blue moves down the column when the column is eluted with water-acetic acid (70 : 30) as the eluant.

Experiment No. 9 : Resolution of racemic mixture of mandelic acid by column chromatography.

Hesse and Hagel method¹.

Principle :

Racemic mixture of mandelic acid can be resolved by column chromatography using a chiral adsorbent material as the stationary phase, e.g., microcrystalline cellulose triacetate (MCCT) i.e., microcrystalline triacetyl cellulose (MCTC), obtained by heterogeneous acetylation of cellulose. In the asymmetric environment, the conditions for inclusion of the two mirror image isomers of a chiral molecule between the laminae of the chiral adsorbent are very different, so that one of the antipodes is preferentially bonded. By selection of a suitable solvent, the bonding becomes reversible and a sorption equilibrium is established upon which a chromatographic separation system can be based. With such a

system, significant separation of racemic mixtures into their antipodes can be achieved. The separation is even more effective if one of the substituents at the asymmetric centre is an aromatic nucleus, as is mandelic acid, $C_6H_5CH(OH)COOH$, since the aromatic ring is jammed in the niches between every two acetylated glucose units in a defined position. Thus, under favorable circumstances, complete separation of racemates can be achieved even with short columns.

Satisfactory results are obtained with water – ethanol (2 : 1) mixture as the eluant. The (+) form is eluted first, the (-) form appears next.

Materials and Apparatus required :

- | | |
|--|---------------------------|
| 1) Microcrystalline cellulose triacetate (71-56 μ M) | 6) Cotton |
| 2) Racemic mandelic acid | 7) Dropper |
| 3) Stand and clamp | 8) Conical flasks (50 ml) |
| 4) Ethanol | 9) Polarimeter |
| 5) Glass chromatography column
(50 cm long and ~1.5-3 cm inner diameter). | |

Procedure :

Secure the glass chromatography column to a stand using a clamp. Place a small wisp of cotton at the bottom of the column using a long piece of glass rod. Add cellulose triacetate to fill up about 30-40 cm of the column. Keep the stopper open and place a 50 ml conical flask underneath the column. Dissolve the racemic mandelic acid (~250 mg) in minimum volume of 95% ethanol. Add this solution with the help of a dropper at the top of the column and allow the solution to run down completely. Now add 5 ml of (2 : 1) water-ethanol mixture and allow it to pass through the column. When the solvent level is 2-3 mm above the surface of the column, add more eluant and elute slowly and continually at a flow rate of ~ 200 ml/ hour keeping the solvent level always above the surface of the column. Collect 20-25 ml portions of the effluent in a series of labelled conical flasks (~50 ml). Monitor each fraction polarimetrically to observe the rotation. Mix together the fractions showing same sign of rotation and evaporate the solutions on a hot water bath to small volumes and crystallise to obtain (+) and (-) forms of mandelic separately.

Reference : 1. Gerhard Hesse and Rainer Hagel,

Justus Liebigs Ann. Chem. 1976, 996-1008.

(d) Paper Chromatographic Separation of Inorganic Ions

Experiment No. 10 : Separation of inorganic ions by paper chromatography

Principle :

In chromatographic separation on paper (cellulose), the materials to be separated undergo partition between the aqueous phase held in the inert cellulose matrix and the mobile phase (organic solvent) analogous to solvent extraction. The more soluble component of the mixture, which is more soluble in organic solvent, distributes more in this solvent relative to the aqueous phase and shows higher R_f value. Similarly the component having lower solubility in the organic solvent shows lower R_f value. Thus, the R_f value is characteristic of a particular species in a given type of chromatographic separation and may be used for qualitative identification of unknown solutes.

In inorganic separation by paper chromatographic technique in the presence of organic developing solvents or mixture of organic solvents, the mobilities of different ions are influenced by solubilities of the inorganic solutes (I) in organic phase (leads to higher R_f values), and (ii) in aqueous phase due to the formation of water-soluble anionic complexes (leading to lower R_f values). In oxygen-containing solvents in the presence of a small amount of HCl, certain metal ions form chlorocomplexes which are soluble in organic solvents. Thus, Fe^{3+} ion readily ascends with the organic solvents containing HCl, whereas, Ni^{2+} does not move appreciably. This makes possible the separation of the two from a mixture. This is due to the fact that under this condition Fe^{3+} forms the complex $[\text{FeCl}_4]^-$ which being a covalent species is more soluble in organic solvent used as developer. Ni^{2+} does not form such chlorocomplex under the same condition. Co^{2+} and Cu^{2+} also form chlorocomplexes that are more soluble in organic solvents. Inorganic chromatographic separation on cellulose matrix may be effected in two ways, viz., either by the use of paper strips or columns of cellulose pulp. The two systems are similar but the methods of operation are different.

If a very small quantity of the sample solution is placed on one end of an absorbent paper of size 30cm \times 5 cm, made from Whatman No.1 filter paper using a fine capillary, a small patch is formed. The end of the paper strip nearer to the test patch is then immersed in a jar containing the developing solvent and saturated with the solvent vapours and the other end is suspended freely in the jar from a glass hook held inside the lid. The solvent now diffuses through the paper on to the test patch by capillary action effecting separation of the metallic ions. When the solvent front has moved a suitable distance (10-12 cm), the paper strip is removed. On evaporating off the solvent followed by spraying a suitable reagent on the strip, the metal ions give characteristic colour bands and thus the metal ions can be identified.

Materials required :

- a) Stationary phase : Whatman No.1 filter paper strips.
- b) Developing Solvent : Acetone : ethyl acetate : 6M-HCl = 9 : 9 : 2 (by volume).
- c) Spraying reagent : Dissolve 10 mg of rubeanic acid in 10 ml of 95% ethanol.
- d) Standard solutions : Dissolve ~4.5 mg /ml each of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in distilled water, each containing ~1 mg of metal ion per ml of the solution.
- e) Unknown solution : A mixture of any two of the above metal ions.
- f) Developing Jar : A tall jar or a 2-litre measuring cylinder fitted with a rubber bung carrying a hook of glass at the lower end from which the paper strip, made from Whatman No.1 paper, may be suspended.

Procedure :

1. Spotting on paper chromatogram :

Cut a paper strip of proper size (according to the dimension of the jar) from a Whatman No. 1 filter paper sheet. Draw a base line with a pencil above 3 cm from the lower end of the strip. Put four pencil-dots on the base line at equal distances apart and mark them 1,2,3 & 4 respectively. Using separate fine capillary tubes, put separate spots of the three known metal ion solutions and the unknown mixture on the pencil-dots and record their respective positions. Allow the spots to dry in air for about 5 minutes.

2. Setting of paper chromatogram inside the solvent-jar :

Take 25 ml of the solvent mixture into the jar, cover it with the lid, thoroughly swirl the solvent inside and allow to stand for a few minutes. Open the jar and suspend the paper strip into the developing solvent in the jar to a depth of 1 cm keeping the solvent level below the base line avoiding contact of the paper strip with the sides of the jar.

3. Chromatographic separation and identification of metal ions :

Allow the solvent to ascend for two hours and then remove the paper strip. Mark the solvent front with a pencil and dry the paper strip as before. Expose the dried paper strip to NH_3 vapours taken in another jar for 15 minutes to neutralise the acid, then spray on both the sides with the spray reagent and dry the paper strip in air. Ni^{2+} gives blue – purple band, Co^{2+} gives yellow – orange band while olive– green band indicates the presence of Cu^{2+} .

4. Measurement of R_f values :

Encircle the developed spots with pencil marks and measure the distances traveled by the metal ions and solvent front from the base line and hence calculate the R_f values and identify the unknown metal ions by comparison with the standards.

Notes :

1. Care must be taken so that the jar becomes saturated with the solvent vapour before introducing the paper strip into the jar.
2. The spot should be made carefully on the paper with a fine capillary.
3. Care must be taken so that the paper strip does not touch the sides of the jar.
4. The paper strip should be suspended from the glass hook into the solvent to a depth of ~ 1- 1.5-cm but the solvent level must be below the starting pencil line.

(e) Experiments based on ion-exchange chromatography

Experiment-11 : Determination of ion exchange capacity of a strongly acidic cation exchange resin by column method

Principle :

Synthetic ion-exchange resins are high molecular-weight polymeric materials containing number of ion-active functional groups. The ion exchange capacity of a resin is dependent upon the total number of ion-active functional groups per unit weight of the material. The greater is the number of such groups the greater will be the capacity. The *ion exchange capacity* of a resin may be defined as the number of milliequivalents (or millimoles) of a monovalent ion like Na^+ (in case of cation-exchanger) or Cl^- (in case of anion-exchanger) exchanged by one gram of the respective dry resins.

Thus the exchange capacity of a cation exchanger may be measured by determining the number of milliequivalents of sodium ion that are absorbed by one gram of the dry resin in the *hydrogen form*. Strongly acidic cation exchange resins are generally polystyrene sulphonic acid resins and the exchange of Na^+ in may be represented by :



(where R_2 represents polymeric network of the resinanion)

For the determination of exchange capacity of a cation exchange resin, a known quantity of the dry resin is first converted into its H^+ -form. Then a sufficiently large excess of a solution of sodium sulphate solution (~0.25M) is passed through the resin column to displace the H^+ ions quantitatively. The effluent containing total amount of H^+ ions is collected and titrated with a standard NaOH solution using phenolphthalein as indicator. If the strength of the NaOH solution be $x(N)$ and V be the titre value required for neutralisation of H^+ ion

in the effluent and w be the weight in grams of the dry resin, then its ion-exchange capacity C will be given by :

$$C = \left(\frac{xV}{w} \right) \text{ m.equiv.g.}^{-1}$$

Chemicals required :

- Standard (N/20) oxalic acid solution : 0.7-0.8 g. (say, w g) of A.R. oxalic acid per 250 ml solution. Strength = $(w / 0.7879) (N/20)$
- 'Duolite C225' or 'Amberlite IR-120' or Dowex-50 cation exchange resin in hydrogen form.
- ~0.25(M) $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ solution (Formula weight = 322.2): ~20g /250 ml in distilled water.
- (~N/20) NaOH solution : Dissolve 2.0 g of A.R. NaOH in distilled water and dilute to 1 L.
- Phenolphthalein indicator : ~0.5% solution in 1:1 alcohol

Procedure :

1. Drying of resin :

Dry the purified resin in the hydrogen form by placing it in an evaporating dish after covering it with a clock glass rested on two glass rods to protect from contamination of aerial dust. Keep the resin in the warm condition at $25 - 35^\circ\text{C}$ till it becomes free-running.

2. Setting of Resin column :

A simple ion- exchange column may be designed out of a glass tube, 20 cm long and 0.5 cm internal diameter (like a micro-burette tube without the stopcock). The upper ~5 cm

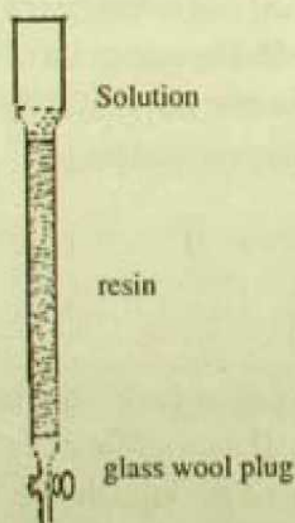


Fig. 8 Ion-exchange column.

portion of the tube should have an internal diameter of ~ 2.5 cm. The lower open end is narrower and is usually attached with a stop-cock or attached to a rubber tubing fitted with a pinchcock after plugging this end with glass wool from the bottom. Weigh out accurately about 0.5 g of the dry resin (in H^+ form) in a 100 ml beaker. At first partially fill the column with double distilled water and remove the air bubbles if any inside the column. Then fill it with the resin suspended in double distilled water and keep the resin covered with double distilled water. Remove the air bubbles sticking to the resin bed. Adjust

the water level to about 1 cm above the surface of resin bed.

3. Standardisation of (~ N/20) NaOH solution :

Pipette out an aliquot of 25ml of the standard (N/20) oxalic acid in a 250ml conical flask, add 25ml of double distilled water and 1-2 drops of phenolphthalein indicator, and titrate with (~ N/20) NaOH solution until a light pink colour appears. Find the strength of the NaOH solution.

4. Elution :

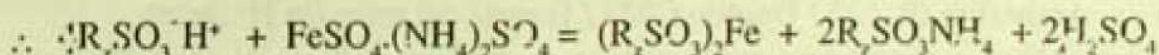
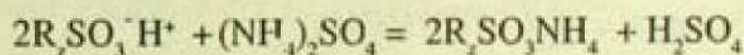
Elute the resin column with 150 ml of ~ 0.25 (M) sodium sulphate solution in portions of 5-10 ml at the rate of 2 ml per minute. Collect the effluent in a 500 ml conical flask. After the completion of elution, wash the bed 4 - 5 times with 4 - 5 ml portions of double distilled water and collect the washings in the same conical flask. Titrate the effluent with the same standard (~N/20) NaOH solution using 1-2 drops of phenolphthalein indicator as before.

Note : The exchange of H^+ ions by Na^+ ions is quantitative because a large excess of eluant (sodium sulphate solution) is allowed to pass through the column.

Experiment No. 12 : Determination of Strength of Mohr's Salt solution by using a strongly acidic cation exchange resin in H^+ form.

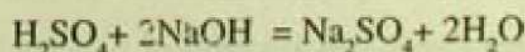
Theory :

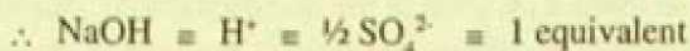
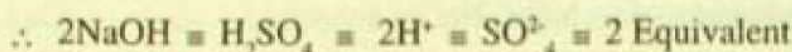
Strongly acidic cation exchange resins are generally polystyrene sulphonic acid resins. When a solution of Mohr's salt, $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$ (formula weight : 392.143) in dil. H_2SO_4 of known concentration is allowed to pass through a resin column in the H^+ form, an equivalent amount of H^+ ion is released from the resin. The ion exchange equilibria may be represented by :



(where R_2 represents the polymeric anion of the resin)

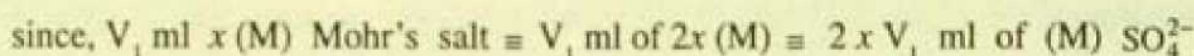
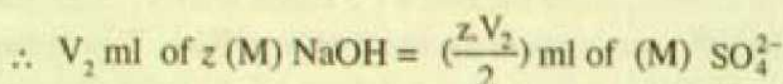
The effluent containing H_2SO_4 , equivalent to $(Fe^{2+} + 2NH_4^+)$ plus the amount present in the medium is collected and titrated with a standard NaOH solution using phenolphthalein as indicator.





Calculation :

If the experimental solution is x (M) in Mohr's salt, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ ($2\text{NH}_4^+ \equiv \text{SO}_4^{2-}$ and $\text{Fe}^{2+} \equiv \text{SO}_4^{2-}$) and y (M) in H_2SO_4 and if V_1 ml of this solution after passing through the cation exchanger in H^+ -form consumes V_2 ml of z (M) NaOH , then,



$$\therefore 2xV_1 + yV_1 = \frac{zV_2}{2}$$

$$\therefore x = \left(\frac{\frac{zV_2}{2} - yV_1}{2V_1} \right) \text{ (M)}$$

$$\therefore \text{Strength of Mohr's salt in g.lit}^{-1} = x \times .392.143$$

Since, V_1 , y and z are known, and V_2 is experimentally determined, therefore x may be calculated.

Chemicals required :

- Standard ($\sim \text{N}/50$) oxalic acid solution : 0.3152 g (w.g. say) A.R. oxalic acid per 250 ml solution. Strength = (w/0.3152) ($\text{N}/50$)
- Amberlite IR-120 / Duolite C225 / Dowex-50 resin (in H^+ form)
- Approx. ($\sim \text{N}/50$) NaOH solution : 0.8-1.0 g.lit⁻¹ in distilled water.
- ($\sim \text{M}/50$) H_2SO_4 : ~ 1.0 ml of (A.R.) conc. H_2SO_4 per litre. Determine the strength of the acid by titrating against standard ($\sim \text{N}/50$) NaOH solution.
- ($\sim \text{M}/50$) Mohr's salt solution (unknown) : Dissolve ~ 4 g (exactly 3.9214 of Mohr's salt in ($\text{M}/50$) H_2SO_4 and dilute to 1 litre with the same acid.
- Phenolphthalein indicator : $\sim 0.5\%$ in 1:1 alcohol

Procedure :

1. Standardisation of NaOH solution :

Pipette out 25ml of the standard (N/50) oxalic acid in a 250ml conical flask and add 1-2 drops of phenolphthalein indicator. Titrate the solution with the (~N/50) NaOH solution until a light pink colour appears. (titre = V ml)

$$V(\text{NaOH}) \times S(\text{NaOH}) = 25 \times (w/0.3152) (N/50)$$

$$\therefore S(\text{NaOH}) = \left(\frac{25 \times w}{V(\text{NaOH}) \times 0.3152} \right) (N/50) = z(N) = z(M)$$

2. Strength of medium H_2SO_4 solution :

Titrate 10 ml of the medium H_2SO_4 solution (~M/50) i.e., (~N/25) used for preparation of the Mohr's salt solution with the standard (~N/50) NaOH solution using phenolphthalein indicator up to a pink end point. (titre = V' ml).

$$10 \times S(\text{H}_2\text{SO}_4) = V' (\text{NaOH}) \times z(N).$$

$$\therefore S(\text{H}_2\text{SO}_4) = \frac{V' (\text{NaOH}) \cdot z}{10} (N) = \frac{V' \cdot z}{20} (M) = y(M).$$

3. Preparation of resin column :

A ion - exchange column consists of 25 -30 cm long, 1.0 -1.5 cm internal diameter glass tube fitted with a stop cock. Internal diameter of the upper portion should be ~2.5 cm. A glass-wool plug is to be fitted at the constricted end. Fill the column with water, remove air bubbles if any and then introduce the resin suspended in distilled water. Remove the air bubbles sticking to the resin bed by stirring with a long glass rod if necessary. Cover the resin-bed with distilled water. The resin column should be 15-20 cm in length. Adjust the water level to about 1-2 cm above the surface of resin bed.

4. Elution :

Wash the column with deionised water to make it acid free (test with indicator paper or pH paper) and adjust the flow rate to ~20 drops per minute. Place a 250 ml conical flask under the column. Pass 5 ml (V_1 ml) of the supplied Mohr's salt solution (M/50) in (M/50) here y(M) H_2SO_4 into the resin column by means of a pipette. Wash the bed with 5 ml portions of deionised water maintaining same flow rate till the washings are free from acid (about 8-10 times) and collect the washings in the same conical flask.

Titrate the combined effluent and the washings with the standardised (N/50) NaOH

solution using phenolphthalein as indicator up to a pink end point. (titre = V_2 ml).

5. Calculate the strength of Mohr's salts (in g per lit) in the supplied solution.

Notes :

1. The resin is to be regenerated after use by eluting 5-6 times with $\sim 2(N)$ HCl adding ~ 5 ml portions at a time followed by washing for 8-10 times with ~ 5 ml portions of distilled/deionised water until acid-free.
2. The liquid level must always be kept at least 1-2 cm above the resin bed during any operation and preservation of the column.
3. Care must be taken to ensure that no air bubble sticks to the resin bed.

Chapter - 9

Physico-Chemical Experiments

Experiment – 1 : Determination of solubility of a given substance in water at different temperatures and construction of its solubility curve.

Theory :

Solubility of a substance in a given liquid, at a specified temperature, is the amount (in grams) of solute required to saturate 100 grams of the solvent to produce a saturated solution which remains in equilibrium with the undissolved solute. If a be the solubility of a solute, then the concentration of its saturated solution at a specified temperature is $10 a/M$ molal, where, M is the molar mass of the solute. For a solid (s) solute, the following equilibrium prevails for a saturated aqueous solution (aq) in contact with some undissolved solute :



The equilibrium constant, K_s , for the dissolution process is given by,

$$K_s = \frac{a_A(aq)}{a_A(s)}$$

where, a 's stand for activity. Since $a_A(s)$ is unity by definition, for a pure solid, $K_s = a_A(aq)$. For a dilute solution, activity coefficients tend to unity, activity may be replaced by the (numerical value) of molar concentration, thus, $K_s = C_A(aq)$. For a dilute solution the molar concentration, C , and molal concentration C_m are very nearly equal and thus,

$$K_s = C_{m_A}(aq)$$

$$K_s = \frac{10 a}{M}$$

where, a , is the solubility of the solute.

The value of the equilibrium constant and hence the solubility is influenced considerably by temperature and pressure according to the Le Chatelier principle. If the volume decreases during dissolution, then an increase of pressure increases the solubility, and vice-versa. If the dissolution process is endothermic, then increase of temperature increases the solubility and vice-versa. Solubility of a substance remains unchanged at different pressures and different temperatures only when the dissolution process is *isochoric* and *isenthalpic*.

The variation of solubility with temperature is represented by *solubility curve*, which is obtained by plotting the solubility along the ordinate (y-axis) and temperature along the abscissa (x-axis). Solubility is experimentally determined either gravimetrically or volumetrically (titrimetrically) using standard procedures.

Solubility curves may be of four types :

- (i) monotonically increasing, usually non-linear curves (e.g. KNO_3),
- (ii) monotonically decreasing usually non-linear (e.g. Ca(OH)_2),
- (iii) straight line parallel to the temperature axis (e.g. NaCl),
- (iv) increasing and then decreasing with a sharp turning point (Na_2SO_4 in its two forms Na_2SO_4 and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$).

Procedure :

Preparation of saturated solutions of the given substances in water, at different temperatures ($T_{\text{room}} < T_1 < T_2$ at $\sim 5^\circ\text{C}$ interval) and estimation of solubilities by different titrimetric procedures (acidimetry, alkalimetry, iodometry etc.).

- (i) Take 100 ml of distilled water and shake with requisite amount of the solid solute \sim twice the solubility to produce a saturated solution at the experimental temperature. Use a thermostat to maintain the temperature fixed.
- (ii) Pipette out aliquot portions (10 ml or 25 ml) from the saturated solution, taking care that no solid particles of the solute are present. This may be ensured by using a pipette with the tip suitably plugged with cotton wool. Introduce the aliquot portions immediately into 100 ml of water in 250 ml conical flasks and shake to mix uniformly. Titrate these diluted solutions against standard solution of the specific reagent using appropriate indicator. Calculate solubility accordingly.

Approximate volume (titre) of different titrants required for 25 ml of saturated solutions of some common substances at 30°C are given below.

Substance	Titrant	Titre	Indicator
Calcium hydroxide	(N/25) HCl	25 ml	Phenolphthalein
Benzoic acid	(N/25) NaOH	20 ml	"
Salicylic acid	"	12.5 ml	"
Potassium hydrogen tartrate	"	32.5 ml	"
Iodine	(N/100) $\text{Na}_2\text{S}_2\text{O}_3$	10 ml	Starch solution

- (iii) Repeat the procedure (i) and (ii) at 3-4 other temperatures higher than the room temperature and determine the solubilities.
- (iv) Construct the solubility curve by plotting solubility against temperature.

Experiment No. 2 : Determination of surface tension of a given liquid/solution by drop weight method using stalagmometer.

Theory :

In a liquid, the molecules attract one another. As a result of this intermolecular attraction, a molecule in the bulk of the liquid suffers zero resultant force, whereas, a molecule at the surface suffers a net resultant force of attraction towards the bulk. The surface of a liquid behaves as a stretched membrane and liquids at rest possess a physical property called surface tension. *Surface tension* of a liquid at a particular temperature is defined as the force acting tangentially across the surface and at right angles to any line of unit length on it. The surface tension may alternatively be defined as the work done in increasing the surface area of the liquid by unity. The unit of surface tension is dyn.cm^{-1} (c.g.s.), or, N.m^{-1} (SI). Surface tension of a liquid depends upon temperature, it decreases as temperature increases and vanishes at the critical temperature of the liquid.

The basis of determining surface tension (γ) of a liquid using a stalagmometer is as follows. When a liquid flows slowly out of the orifice of a capillary tube under the action of gravity, the balance of force just at the point of detachment of the spherical drop may be expressed by equation (1) (neglecting the buoyancy effects of surrounding air medium)

$$mg = 2 \pi r \gamma \Phi \quad \dots \quad \dots \quad \dots \quad \dots \quad (1)$$

where, m = mass of a drop, g = acceleration due to gravity, r = radius of the capillary, γ = surface tension of the liquid, Φ = Harkins-Brown correction factor for the instrument.

If a definite volume (V) of two liquids (1 and 2) of density d_1 and d_2 and surface tension γ_1 and γ_2 on passing through a uniform capillary tube (stalagmometer) produces respectively n_1 and n_2 number of drops, applying the relation (1) one may obtain,

$$\frac{\gamma_1}{\gamma_2} = \frac{(V/n_1)d_1}{(V/n_2)d_2} = \frac{n_2}{n_1} \cdot \frac{d_1}{d_2} \quad \dots \quad \dots \quad \dots \quad \dots \quad (2)$$

Thus, by counting the number of drops produced from a fixed volume of two liquids and determining the ratio of their densities one may compare their surface tensions. If the surface tension of one of the liquids, (reference liquid, e.g. water) is known (γ_w), then the surface tension (γ_l) of another liquid can be obtained using the relation :

$$\frac{\gamma_L}{\gamma_w} = \frac{n_w}{n_L} \cdot \frac{d_L}{d_w} = \frac{n_w}{n_L} \cdot S_L \quad \dots\dots\dots (3)$$

where, S_L = specific gravity of the liquid.

$$\therefore \gamma_L = \left(\frac{n_w}{n_L} \right) \cdot S_L \cdot \gamma_w \quad \dots\dots\dots (4)$$

Thus, by counting the number of drops produced by passing a definite volume of water and the liquid, or, solution and determining its specific gravity, surface tension (γ_L) can be calculated using the surface tension (γ_w) of water at the same temperature.

Procedure :

1. Determine the specific gravity (S_L) of the solution / liquid by usual procedure (using specific gravity bottle).
2. Rinse the stalagmometer with distilled water thoroughly. Suck in fresh distilled water and adjust the number of drops falling per minute between 10 to 15. Suck in water again, release and start counting the number of drops as the meniscus touches the upper graduation mark and stop when it touches the lower mark. Repeat the counting twice more and record the number of drops (n_w).
3. Repeat the process (2) with the supplied solution/liquid and record the number of drops (n_L).
4. Calculate the surface tension of the solution using the relation (4).

Experiment No. 3 : Determination of viscosity coefficient of a given liquid / solution with Ostwald viscometer.

Theory :

Viscosity is the property, which, opposes the relative motion of adjacent portions of a liquid and can be regarded as a type of internal friction. *Newton's law* of viscous force is applicable when a liquid flows slowly and executes streamlined motion. The law states that, the force (f) required to maintain a velocity difference of, dV_x (in the x-direction) between two parallel layers of area, A , separated by a distance of dz in the z-direction) is given by :

$$f = \eta A \frac{dV_x}{dz} \quad \dots\dots\dots (1)$$

where, (η) is the *viscosity coefficient* of the liquid which is defined as the force per unit

area required to maintain a unit velocity gradient (in the x-direction). The (c.g.s.) unit of η is *poise* and 1 poise = 1. dyne.sec.cm⁻². The magnitude of η depends up on temperature. η decreases by about 2% per degree Celsius rise in temperature.

The viscosity coefficient (η) may be determined experimentally using an Ostwald viscometer which utilizes the Poiseuille equation,

$$\eta = \frac{\pi r^4 t P}{8 v l} \quad \dots\dots \quad (2)$$

This equation is valid for an incompressible fluid (i.e. a liquid) flowing very slowly (streamlined motion) through a narrow tube of radius, r , and length, l , under an average pressure of P , when there is a flow of v volume of the liquid in time t .

If t_1 and t_2 be the times of fall of a definite volume of two liquids (1 and 2) through the Ostwald viscometer and η_1 and η_2 be their viscosity coefficients, and P_1 and P_2 respectively be the average pressures, then one may obtain from eqn. (2).

$$\frac{\eta_1}{\eta_2} = \frac{P_1 t_1}{P_2 t_2} \quad \dots\dots \quad (3)$$

The pressure P , driving the liquid through the capillary at any instant, is equal to $h d g$, where, h is the difference in height between the levels of the liquid in the two limbs, d is the density of the liquid and, g is the acceleration due to gravity. During the experiment, P decreases with time as h decreases. The initial height difference (h_1) and the final height difference (h_2), ($h_1 > h_2$), are same for both the liquids, since the same volumes of the two liquids are allowed to pass through the capillary tube. Thus, the average pressures P_1 and P_2 may be expressed as :

$$P_1 = [(h_1 + h_2)/2] \cdot d_1 \cdot g$$

$$\text{and } P_2 = [(h_1 + h_2)/2] \cdot d_2 \cdot g$$

$$\text{Thus, } \frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2} \quad \dots\dots \quad (4)$$

In the Ostwald viscometer a definite volume of a reference liquid (water) is introduced in the wider arm of the instrument. The liquid is sucked into the narrower arm and the time required for a fixed volume of the liquid to flow through the capillary under the action of gravity is noted. The procedure is repeated for the experimental liquid (L).

When water (w) is used as the reference liquid, the expression (4) is transformed to (5)

$$\frac{\eta_L}{\eta_w} = \left(\frac{d_L}{d_w} \right) \left(\frac{t_L}{t_w} \right) = S_L \frac{t_L}{t_w} \quad \dots\dots\dots (5)$$

$$\therefore \eta_L = S_L \left(\frac{t_L}{t_w} \right) \cdot \eta_w \quad \dots\dots\dots (6)$$

where, η_w , η_L , d_w , d_L , t_w , t_L have their usual meanings and S_L is the specific gravity of the liquid. Thus, if the viscosity coefficient (η_w) of water is known, the viscosity coefficient (η_L) of the liquid can be determined by determining the specific gravity (S_L) of the liquid and measuring the times of flow t_w and t_L of definite volumes of water and the liquid respectively.

Procedure :

1. Determine the specific gravity of the supplied solution / liquid by usual procedure (using a specific gravity bottle).
2. Rinse the Ostwald's viscometer with distilled water and drain out the water thoroughly. Add a measured volume of water (using a pipette) into the wider limb of the viscometer and clamp it vertically. Suck in the water, release it and start the stopwatch as the meniscus touches the upper mark of the narrower limb and stop the stopwatch as the meniscus touches the lower mark of the same limb. Repeat this process twice more and record the time of flow.
3. Repeat the process 2 with the supplied solution/liquid and calculate the viscosity coefficient of the supplied solution/liquid accordingly.

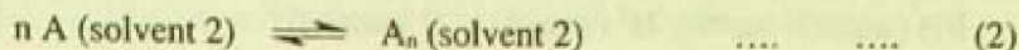
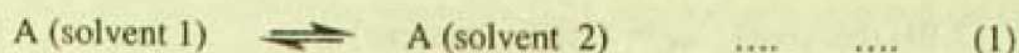
Experiment No. 4 : Determination of distribution coefficient of an organic acid between water and an organic solvent.

Theory :

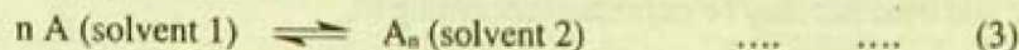
According to *Nernst distribution law*, when a substance is allowed to equilibrate with a mixture of two immiscible liquids in which the substance is soluble, it will distribute itself between the two solvents in such a way that at equilibrium the ratio of the concentrations of the solute in the two liquids is constant at constant temperature, provided that there is neither association nor dissociation of the solute in the two solvents and there is no chemical reaction between the solute and the solvents or between the solvents. This constant is called the *distribution coefficient* of the solute between the two solvent.

When a solute, A, remains monomeric in one solvent (solvent – 1), but undergoes

association to polymeric species, A_n ($n = 1, 2, 3, \dots$), in another solvent (solvent - 2), the following distribution equilibria are established when A is allowed to equilibrate between solvent-1 and solvent-2.



The overall distribution equilibrium is, therefore,



for which the overall distribution equilibrium constant (K_d) is given by the activity quotient,

$$K_d = \frac{(a_{A_n})_2}{(a_A)_1^n} \quad \dots \quad \dots \quad (4)$$

where, the right subscripts 1 and 2 represent solvent 1 and solvent 2 respectively and a 's stand for activities of the respective species. Activities (a) are related to molar concentrations (c) through the activity coefficients (f) according to $a = c.f$. In dilute solutions, activity coefficients are very close to unity, so the activities approach numerical values of the molar concentrations (as $f \rightarrow 1$, $a \rightarrow c$). For a dilute solution, the equilibrium constant, K_d may be expressed as concentration quotient according to,

$$K_d = \frac{(C_{A_n})_2}{(C_A)_1^n} \quad \dots \quad \dots \quad (5)$$

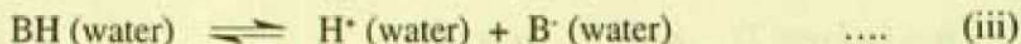
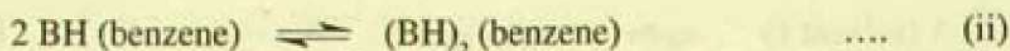
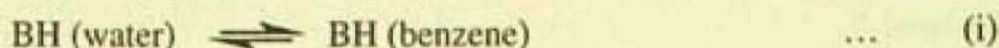
If the total concentration of A in solvent 1 is C_1 , and the total concentration of A in solvent 2 is C_2 and if all the molecules of A in solvent 2 are present as A_n then, $(C_A)_1 = C_1$ and $(C_{A_n})_2 = C_2$. So the eqn. (5) is simplified to,

$$K_d = \frac{C_2}{C_1^n} \quad \dots \quad \dots \quad (6)$$

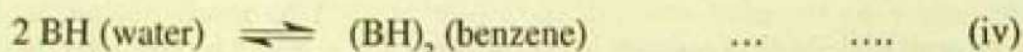
$$\log K_d = \log C_2 - n \log C_1 \quad \dots \quad \dots \quad (7)$$

Thus the distribution equilibrium constant, K_d , and the degree of association, n , can be found out if two sets of values of the concentration terms C_1 and C_2 are experimentally determined.

Benzoic acid (C_6H_5COOH , BH) distributes between water and benzene. It undergoes dimerization in benzene, and in water, it ionizes as a very weak acid according to,



Neglecting the ionization in water, the overall distribution equilibria of benzoic acid between water and benzene may be expressed according to,



of which the overall distribution equilibrium constant, K_d , will be given by

$$K_d = \frac{C_{(BH)_2 \text{ (benzene)}}}{C_{BH \text{ (water)}}^2} = \frac{C_b}{C_w^2} \quad \dots \quad (v)$$

where, C_w = concentration of BH in water and C_b = concentration of BH in benzene at equilibrium. Thus,

$$\log K_d = \log C_b - 2 \log C_w \quad \dots \quad (vi)$$

$$\therefore \log C_b = \log K_d + 2 \log C_w \quad \dots \quad (vii)$$

Thus a plot $\log C_b$ vs. $\log C_w$ will be a straight line of slope = 2 and intercept = $\log K_d$. By measuring the concentrations (C_w and C_b) of benzoic acid in water and benzene in a series of mixtures of water and benzene in different proportions, it is possible to determine K_d and also the degree of association, ($n \approx 2$), at room temperature.

Procedure :

1. Prepare 100 ml of a standard ($\sim N/20$) oxalic acid solution by accurate weighing.
2. Prepare 250 ml of a ($\sim N/20$) NaOH solution and standardise the same against standard ($N/20$) oxalic acid solution using phenolphthalein as indicator.
3. Prepare 4 (four) sets of mixtures of the following compositions in 250 ml stoppered glass bottles keeping the total volume fixed.

Set	I	II	III	IV
Volume (ml) of benzoic acid solution (in benzene)	10	20	30	40
Volume (ml) of benzene	40	30	20	10
Volume (ml) of water	100	100	100	100

4. Shake the mixtures in the stoppered bottles thoroughly for 45 minutes and then allow to settle till the phases separate clearly.
5. For titration of the organic layer take an aliquot of 5 ml (**using a mechanical sucking pipette**), add ~40 ml water (two test-tubes full). Shake thoroughly and titrate with the standard (~N/20) NaOH solution using phenolphthalein as indicator. Compute the value of C_b , the concentration of benzoic acid in benzene layer.
6. For titration of the aqueous layer take an aliquot of 25 ml (**using a mechanical sucking pipette**) and titrate it against the same standard (~ N20) NaOH solution using phenolphthalein as indicator. Compute the value of C_w , the concentration of benzoic acid in water layer.
7. Perform the experiments (5) and (6) for all the four sets.
8. (i) Calculate the quantities C_b / C_w and $\sqrt{C_b} / C_w$ at room temperature and interpret the results.
(ii) Plot $\log C_b$ vs. $\log C_w$, draw the best straight line through the experimental points and find the slope and $\log K_d$ from the intercept.

Note : Benzene is highly inflammable and toxic. It should be handled with extreme care. It should not be pipetted out by mouth suction and it should not be inhaled.

Experiment 5 : To determine the pH of a given buffer solution by colour matching of indicator.

Theory :

The pH of an aqueous solution is the negative of logarithm to base 10 (\log_{10}) of hydrogen ion activity (a_{H^+})

$$pH = - \log_{10} a_{H^+} \quad \dots \quad \dots \quad \dots \quad (1)$$

For dilute solutions, activity coefficients (f) are nearly unity, and so the activity may be replaced by the numerical value of the molar concentration (c) (since $a = c.f$; as $f \rightarrow 1$, $a \rightarrow c$). For such a dilute solution,

$$pH = - \log_{10} c_{H^+} \quad \dots \quad \dots \quad \dots \quad (2)$$

A buffer solution is a mixture of a weak acid and its salt or of a weak base and its salt. pH of buffer solutions have definite values depending upon the ionization constants (pK 's) of the constituent acids or bases and the ratios of acid : salt or base : salt as the case

may be. Buffer solutions have the ability to resist the change of pH when small amounts of acids and bases are added to them.

pH of a buffer solution consisting of a weak acid and its salt with a strong base is expressed by the *Henderson equation* :

$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]} \quad \dots\dots\dots (3)$$

where, K_a is the ionisation constant of the weak acid and []'s represent the molar concentrations. Thus, a series of buffer solutions of known pH values may be obtained by mixing known amounts of a weak acid with known amounts of its salt.

Acid-base indicators exhibit distinguishable colours in distinctly acidic and distinctly alkaline solutions, the actual shade of colour, of course, depends up on the ratio of the concentrations of the acidic and basic forms of the indicator, which in turn depends upon the pH of the solution. An acid-base indicator (HIn) ionises according to,



for which the ionisation constant, K_{in} , is given by

$$K_{in} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]} \quad \dots\dots\dots (5)$$

since, HIn and In^- have distinctly different colours depending upon their concentrations and pH of the solution, the ionisation constant, K_{in} , of the indicator may be expressed according to,

$$K_{in} = \frac{[\text{H}^+][\text{In}^-]_{\text{colour}}}{[\text{HIn}]_{\text{colour}}} \quad \dots\dots\dots (6)$$

$$\therefore \text{pH} = \text{pK}_{in} + \log \frac{[\text{In}^-]_{\text{colour}}}{[\text{HIn}]_{\text{colour}}} \quad \dots\dots\dots (7)$$

Since, human eye can recognise one colour distinctly when its intensity is 10 times higher than that of other colours, the indicator will show the colour of its acid form (HIn) when $[\text{HIn}] \geq 10 [\text{In}^-]$ and it will show the colour of its basic form (In^-) when $[\text{In}^-] \geq 10 [\text{HIn}]$. That is, the colour change interval of the indicator will be :

$[\text{HIn}] \geq 10 [\text{In}^-]$	$\text{pH} = \text{pK}_{in} - 1$	colour of HIn
$[\text{In}^-] \geq 10 [\text{HIn}]$	$\text{pH} = \text{pK}_{in} + 1$	colour of In^-

When the pH of the buffer solution is in range : $(pK_{in} - 1) < pH < (pK_{in} + 1)$, the indicator will show a mixed colour depending upon the pH of the buffer solution as determined by the ratio of concentrations of the weak acid to that of its salt, $([acid] / [salt])$. Therefore, the pH of an unknown solution can be determined by colour matching of the indicator when the same amount of the indicator is placed in the same volume of a series of buffer solutions of known pH values and same volume of the unknown solution, provided the pH of the unknown solution falls within the range : $(pK_{in} - 1) < pH < (pK_{in} + 1)$ and pK_a of the weak acid falls within $pH \pm 1$ of the unknown solution.

Procedure : (For acetic acid-acetate buffer, pK_a of acetic acid = 4.74 at 25°C)

- 1) Prepare 200 ml of ~ 0.4(N) acetic acid solution
- 2) Prepare 200 ml of ~ 0.5 (N) NaOH solution.
- 3) Standardize the prepared ~ 0.5 (N) NaOH solution against the 0.4 (N) acetic acid solution, taking 10 ml of the acid as aliquot and titrating with the NaOH solution using phenolphthalein as indicator.
- 4) Find the strength of the alkali solution and prepare 100 ml of 0.4(N) NaOH solution by exact dilution of the ~ 0.5(N) solution using a burette.
- 5) Take 10 hard glass test-tubes (20 ml) of approximately equal diameter, label them with 1 to 9 and prepare the buffer solutions of following compositions and mix uniformly.

Test-tube No.	Volume of 0.4(N)CH ₃ COOH (ml)	Vol. of 0.4(N) NaOH (ml)	Vol. Of H ₂ O (ml)	Total Vol. (ml)	pH (experimental)
1	5.0	0.5	4.5	10.0	3.72
2	5.0	1.0	4.0	10.0	4.05
3	5.0	1.5	3.5	10.0	4.27
4	5.0	2.0	3.0	10.0	4.45
5	5.0	2.5	2.5	10.0	4.63
6	5.0	3.0	2.0	10.0	4.80
7	5.0	3.5	1.5	10.0	4.99
8	5.0	4.0	1.0	10.0	5.23
9	5.0	4.5	0.5	10.0	5.57

- 6) In the remaining test-tube marked 10 pipette out exactly 10 ml of the unknown solution.

- 7) To each of these test-tube add 3 drops of the appropriate indicator (pK_{in} close to pK_a of the acid). Mix thoroughly to develop the uniform colour in each test-tube. Match the colour of the unknown solution (10) with the colours of the series of buffer solutions (1-9) and hence find the pH of the unknown solution.

Experiment No. - 6 : To determine the rate constant of a first order reaction (hydrolysis of ester) by titrimetric method.

Theory :

Rate of first order reaction is directly proportional to the first power of the concentration of the reactant. A first order reaction may be represented as,



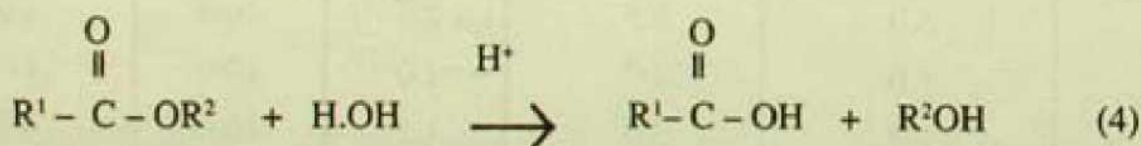
for which the rate,

$$\frac{-dC_A}{dt} = k C_A, \quad \dots \quad \dots \quad \dots \quad (2)$$

where, k , is the rate constant (unit : time^{-1}) and C_A is the molar concentration of A at time t . Integration of the rate equation with proper limits at $t = 0$, $C_A = C_0$ and $t = t$, $C_A = C_t$, converting the logarithmic term to base 10 (i.e., \log_{10}) one obtains,

$$k = \frac{2.303}{t} \log_{10} \frac{C_0}{C_t} \quad \dots \quad \dots \quad \dots \quad (3)$$

Hydrolysis of an ester (R^1COOR^2), although appears to be bimolecular, but it is kinetically a first order reaction with respect to the ester, since, water (H_2O) molecules are present in large excess.



	R^1	R^2
methyl acetate :	CH_3	CH_3
ethyl acetate :	CH_3	C_2H_5

The reaction is slow and is efficiently catalysed by strong acids (say HCl; H^+ is the active ion). When a known amount of an ester (methyl acetate or ethyl acetate) is allowed to hydrolyse in presence of a known amount of strong acid (say, HCl), the progress of the reaction may be studied by withdrawing measured volumes of aliquots from the reaction mixture at different intervals of time and titrating the same with a standard alkali solution using phenolphthalein as indicator. The volume of standard alkali required for a known volume of aliquot at any instant of time is equivalent to the sum of the amount of acetic acid (a weak acid) formed and the amount of strong acid used as the catalyst (a fixed amount). If V_0 , V_t and V_∞ be the volumes of the standard alkali required for the same volume of the aliquots –at the beginning, ($t = 0$), at time t and at the end of the reaction (infinite time, $t = \infty$), then,

$$(V_\infty - V_0) \equiv C_0 \text{ initial amount of the ester} \quad \dots \dots \dots (5)$$

$$(V_t - V_0) \equiv \text{amount of ester consumed} = \text{amount of weak acid formed}$$

$$\text{amount of ester left} \equiv (V_\infty - V_0) - (V_t - V_0) \equiv (V_\infty - V_t) \equiv C_t$$

$$\therefore k = \frac{2.303}{t} \log_{10} \left(\frac{V_\infty - V_0}{V_\infty - V_t} \right) \quad \dots \dots \dots (6)$$

$$\therefore \log_{10} \left(\frac{V_\infty - V_0}{V_\infty - V_t} \right) = \left(\frac{k}{2.303} \right) t$$

Thus, measuring V_0 , V_t and V_∞ and plotting $\log_{10} [(V_\infty - V_0) / (V_\infty - V_t)]$ against t , it is possible to determine k from the slope of the resulting straight line passing through the origin.

$$k = 2.303 \times \text{slope} \quad \dots \dots \dots (7)$$

Note : The experimentally determined rate constant, k , is related to the concentration $[H^+]$ of the acid (catalyst) according to : $k = k_0 [H^+]$, where, k_0 is the rate constant of the uncatalysed reaction.

Procedure :

1. Prepare 250 ml of approximately 0.1 (N) NaOH solution, and 100 ml of ~ 1(N) HCl, or, 100 ml of ~ 0.5(N) HCl solutions. Place all these solutions in the thermostat (or in a large volume of water) maintained at the required temperature.
2. Take 50 ml of the catalyst acid solution (HCl) in a 100 ml dry conical flask placed at the required temperature add 5 ml of the ester using a pipette and note the time of half-discharge and mix uniformly.
3. Immediately after mixing, withdraw, using a pipette, 2 ml of an aliquot from the

reaction mixture into 50 ml of ice-cold distilled water in a 250 ml conical flask, note the time of half-discharge and mix well and titrate immediately against the 0.1 (N) NaOH solution using phenolphthalein as indicator. Take this titre as V_0 .

4. Repeat the step 3 at different time intervals (5, 10, 15, 20, 25 minutes) of time and record the titre (V_t) and time (t) data in a tabular form.
5. After the required titrations are over, place the residual mixture on a hot water-bath and heat at $\sim 60^\circ \text{C}$ for ~ 30 minutes using an air-condenser. Cool to room temperature, take 2 ml of an aliquot into 50 ml of water and titrate against the same 0.1 (N) NaOH solution, using phenolphthalein as indicator as before. This titre gives V_∞ .
6. Plot $\log (V_\infty - V_0) / (V_\infty - V_t)$ vs. time (t) and draw the best straight line passing through the origin and the experimental points and find k from the slope.

Experiment No. – 7 : To determine the solubility product of a sparingly soluble salt by titrimetric method.

Theory :

Solubility of a solute in a solvent at a particular temperature is defined as the number of grams of the solute required to saturate 100 grams of the solvent to produce a saturated solution that remains in equilibrium with undissolved solute. If S_0 be the solubility, then the concentration of the saturated solution is $10 S_0 / M$ molal, where, M is the molar mass of the solute. Saturated solutions of sparingly soluble salts are sufficiently dilute, as such the concentrations in molarity are very close to molality. For such solutions molar concentrations may conveniently be used as the measure of their solubility.

Solubility product of a sparingly soluble electrolyte is the product of the activities of the ions (raised to proper power), remaining in equilibrium with the solid solute in a saturated solution at a particular temperature. Solubility equilibria of a 1:1 sparingly soluble salt, A^+B^- , in aqueous media may be represented according to :



for which the activity solubility product (K_a) and the concentration solubility product (K_c) are defined as

$$K_a = a_{A^+} \text{ (aq)} \times a_{B^-} \text{ (aq)} \dots \dots (1a)$$

$$K_c = [A^+ \text{ (aq)}] \times [B^- \text{ (aq)}] \dots \dots (1b)$$

where, a's represent activities and []'s represent molar concentrations.

Since, activity (a) = [Concentration] \times activity coefficient (f), i.e.,

$$a_{A^+} = [A^+].f_{A^+} \quad \text{and} \quad a_{B^-} = [B^-].f_{B^-}$$

$$\therefore K_s = K_c.(f_{A^+}.f_{B^-}) = K_c.(f_{\pm})^2 \quad \dots \quad (1c)$$

where, (f_{\pm}) is the mean ionic activity coefficient of the electrolyte.

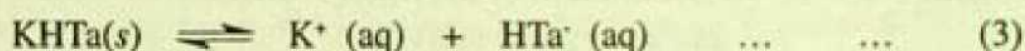
Solubility product is an equilibrium constant at a constant temperature, since activity of the pure solid solute is unity.

As the saturated solution of a sparingly soluble salt is very dilute, the activity of the ions become numerically equal to their molar concentrations since the mean activity coefficient (f_{\pm}) tends to be unity, therefore,

$$K_s = K_c = S_o \times S_o = S_o^2 \quad \dots \quad (2)$$

where, S_o = solubility of the salt (A^+B^-) in moles per litre.

Potassium hydrogen tartarate (KHTa) is a sparingly soluble salt. In aqueous solution it ionises according to,



If the concentration of HTa^- ion in the saturated solution of KHTa in water at room temperature is S mols / litre, then the concentration solubility product, K_c , may be obtained from the relation :

$$K_c = S^2 \quad \dots \quad (4)$$

Solubility (S') of the salt (KHTa) in a solution containing a common ion (e.g. KCl), is lower than that in pure water. Since the solubility product (K_c) is a constant,

$$K_c = (S' + C) S' \quad \dots \quad (5)$$

where, C , is the concentration of the external electrolyte (KCl). In the presence of an electrolyte having no ions in common (eq. NaNO_3), the ionic strength of the medium increases, and the mean ionic activity coefficient decreases (a consequence of *Debye-Huckel limiting law*) and there is a consequent increase of solubility (S) of the sparingly soluble salt. As a result, K_c increases but K_s at a particular temperature remains unchanged.

Procedure :

- 1) (a) Prepare 100 ml of standard (N/20) oxalic acid solution by accurate weighing. Prepare 250 ml of approximately (\sim N/20) NaOH solution and standardise the same against the standard (N/20) oxalic acid solution using phenolphthalein as indicator.

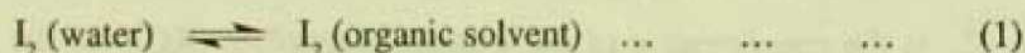
- (b) Prepare 100 ml of (N/20) KCl and 100 ml (N/20) NaNO₃ by accurate weighing.
- 2) In a clean and dry 125 ml stoppered glass bottle take ~ 0.75 g. of the salt (KHTa) and 50 ml of distilled water. Shake the bottle till equilibrium is reached and a saturated solution is obtained. Check that some solid remains undissolved. If necessary add some more solid and shake.
- 3) Perform the step (2) using the solution of the electrolytes (KCl, NaNO₃ etc.) instead of distilled water.
- 4) (a) Dry filter the solution, reject the first few ml of the filtrate and then collect the residual filtrate in a clean dry beaker. Pipette out 10 ml of this filtrate and titrate against the standard ~ (N/20) NaOH solution using phenolphthalein indicator. Repeat the titration twice.
(b) Perform the step 4(a) for the remaining two mixtures.
- 5) Calculate the solubility and solubility product accordingly.

Experiment No. - 8 : Determination of partition coefficient of iodine between water and an organic solvent.

Theory :

According to *Nernst distribution law*, if to a system consisting of two immiscible or slightly miscible liquids is added a third substance, which is soluble in both the liquids, the substance distributes itself between the two liquids in such a manner, that the ratio of its molar concentrations (precisely the activities) in the two liquids remains constant at a particular temperature.

The following equilibrium is established when iodine (I₂) is added to water in presence of an immiscible organic solvent :



Thus If (a_{I₂})_w and (a_{I₂})_o be the activities of the solute (I₂) in the two liquids, water (w) and organic solvent (o) at equilibrium, then,

$$K_d = \frac{(a_{I_2})_o}{(a_{I_2})_w} = \text{constant} \quad \dots \quad \dots \quad (2)$$

The constant, K_d is the *distribution coefficient*, or, the *partition coefficient* of the solute (I₂) between the two liquids, organic solvent and water. This expression holds good

so long as the solute retains the same state of aggregation in the two solvents, i.e., there is neither association nor dissociation of the solute in the two solvents and nor there occurs any chemical reaction between the solute and the solvents nor even between the solvents.

If both the phases are dilute solutions, then, the activity coefficients are very close to unity and molar concentration of the solute (I_2) in the two phases, $[I_2]_w$ and $[I_2]_o$ approach their activities $(a_{I_2})_o$ and $(a_{I_2})_w$ respectively, and distribution coefficient, K_d , is then given by,

$$K_d = \frac{[I_2]_o}{[I_2]_w} \quad \dots \quad \dots \quad \dots \quad (3)$$

Thus, by determining the concentrations of I_2 in the two liquid layers by titrating with a reducing agent, eg., sodium thiosulfate using starch indicator it is possible to determine the value of K_d at room temperature.

Thiosulfate ($S_2O_3^{2-}$) is oxidised by I_2 to tetrathionate ($S_4O_6^{2-}$) according to,



If V_1 ml of the aqueous layer of iodine requires for titration T_1 ml of S (N) thiosulfate solution, and V_2 ml of organic layer of iodine requires T_2 ml of x S(N) thiosulfate solution ($x > 1$), then the partition coefficient, K_d , will be :

$$K_d = \frac{T_2 \cdot x S / V_2}{T_1 \cdot S / V_1} = x \left(\frac{T_2}{T_1} \right) \left(\frac{V_1}{V_2} \right) \quad \dots \quad \dots \quad (5)$$

As for example, if $x = 5$, $V_1 = 25$ ml, $V_2 = 5$ ml, then,

$$K_d = 25 \left(\frac{T_2}{T_1} \right) \quad \dots \quad \dots \quad (6)$$

Procedure :

- 1) Prepare 500 ml ($\sim N/20$) sodium thiosulfate solution. Prepare 250 ml of a ($N/100$) thiosulfate solution by exact dilution of 50 ml of the ($N/20$) solution in a 250 ml volumetric flask.
- 2) Prepare the following two sets in two clean and dry 250 ml stoppered glass bottles

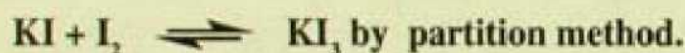
Note : The constancy of K_d follows from the thermodynamic principles that, when two phases of the same substance are in equilibrium at constant temperature and pressure the chemical potential of the dissolved substance will be the same in both phases.

Set	Water (ml)	Solution of Iodine (ml)	Pure Solvent (ml)
I	100	30	0
II	100	15	15

- 3) Shake the bottles thoroughly for about 45 minutes and allow to settle till a clear separation of phases occurs.
- 4) For both sets take 25 ml aliquot for aqueous layer and 5 ml aliquot for organic layer. In case of titration of the organic layer add 40 ml (two test-tubes full) of distilled water and 1g. of KI. Shake well and then titrate.
- 5) Titrate the organic layer with the (N/20) sodium thiosulfate solution and titrate the aqueous layer using the (N/100) thiosulfate solution. Use freshly prepared cold starch solution as indicator. Colour change at the end point will be from intense blue to colourless.

Note : Use a mechanical sucking pipette for transferring the organic layer.

Experiment No. – 9 : To determine the equilibrium constant of the reaction



Theory : In aqueous solution iodine (I_2) reacts with potassium iodide (KI) to produce potassium triiodide (KI_3) according to :



for which the equilibrium constant K is given by

$$K = \frac{\left(a_{\text{I}_3^-} \right)_w}{\left(a_{\text{I}^-} \right)_w \left(a_{\text{I}_2} \right)_w} \quad \dots \quad \dots \quad \dots \quad (1a)$$

where, a's represent the activities of the species at equilibrium, and the subscript 'w' stands for aqueous solution. For dilute solution, the activities (a) are very close to molar

concentrations (since the activity coefficients approach unity) and the equilibrium constant, K , may be expressed in terms of molar concentrations (C) according to :

$$K = \frac{(C_{I_2})_w}{(C_{I^-})_w (C_{I_2})_w} \quad \dots \quad \dots \quad (1b)$$

The equilibrium concentration of I_2 in aqueous solution, $[I_2]_w$, may be obtained from the partition coefficient by the application of Nernst distribution law, which states that when a solute is in contact with two immiscible solvents, the solute distributes itself between the two solvents in such a way that at equilibrium the ratio of the activities (i.e., molar concentrations, for dilute solutions) of the solute in the two solvents is a constant, at a particular temperature, called the partition coefficient or the distribution coefficient (K_d). Thus, when the solute iodine is in equilibrium with water (w) and an immiscible organic solvent (o), the partition coefficient, K_d , may be expressed according to :

$$K_d = \frac{(C_{I_2})_o}{(C_{I_2})_w} \quad \dots \quad \dots \quad (2)$$

$$\therefore (C_{I_2})_w = \frac{(C_{I_2})_o}{K_d} \quad \dots \quad \dots \quad (2a)$$

If C = total concentration of KI (i.e., I^-) initially present,

C_w = total concentration of iodine (i.e., free I_2 + I_2^-) in aqueous layer at equilibrium, then,

$$(C_{I_2^-})_w = C_w - (C_{I_2})_w = C_w - \frac{(C_{I_2})_o}{K_d} \quad \dots \quad \dots \quad \dots \quad (3)$$

$$C = (C_{I^-})_w + (C_{I_2^-})_w$$

$$\therefore (C_{I^-})_w = C - (C_{I_2^-})_w = C - \left[C_w - \frac{(C_{I_2})_o}{K_d} \right] \quad \dots \quad \dots \quad (4)$$

Thus, the working expression for the equilibrium constant, K , becomes,

$$K = \frac{\left[C_w - \frac{(C_{I_2})_o}{K_d} \right]}{\left[C - (C_w - \frac{(C_{I_2})_o}{K_d}) \right] \left[\frac{(C_{I_2})_o}{K_d} \right]} \quad \dots \quad (5)$$

Procedure :

1. Prepare 250 ml of standard (N/20) $K_2Cr_2O_7$ solution and 250 ml of standard (N/20) KI solution by accurate weighing.
2. Prepare 500 ml (~ N/20) sodium thiosulfate solution and standardise the same against the standard (N/20) $K_2Cr_2O_7$ solution iodometrically using starch indicator following the usual procedure.
3. Prepare 4 (four) experimental sets of following compositions in 250 ml stoppered glass bottles :

Set	I	II	III	IV
Volume (ml) of KI solution	10	20	30	40
Volume (ml) of Iodine solution in organic solvent	40	40	40	40
Volume (ml) of Water	90	80	70	60

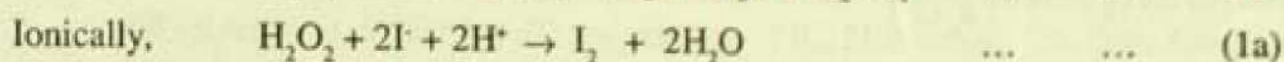
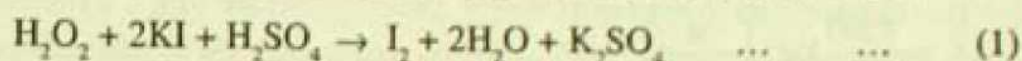
4. Stopper the glass bottles properly and shake the mixtures thoroughly for 45 minutes and allow to settle till a clear separation of the two phases occurs.
5. For the determination of partition coefficient (K_d), follow the procedure as described in experiment No. 8.
6. For titration of I_2 in the organic layer take an aliquot of 10 ml (using a **mechanical** sucking pipette), add 40 ml (two test-tubes full) of water, 1g. of KI. Shake thoroughly and titrate with the standard (~N/20) thiosulfate solution using starch indicator. Estimate the concentration of iodine in organic layer and find $(C_{I_2})_o$.
7. For titration of iodine in the aqueous layer, take an aliquot of 10 ml (using a suction pipette) add 40 ml (2 test-tubes full) of water and titrate with the standard (N/20)

thiosulfate solution using starch indicator and find C_w , the concentration of iodine in water layer.

8. Calculate the value of K at room temperature, using the value of the partition coefficient, K_d , and interpret the results.

Experiment No. – 10 : To determine the rate constant of decomposition of H_2O_2 by acidified KI solution using clock reaction.

Theory : In dilute acid medium (dil. H_2SO_4) H_2O_2 reacts with KI according to



The overall reaction is kinetically of second order, being first order in H_2O_2 and first order in I^- . The rate of the reaction may be expressed according to :

$$\text{rate} = \frac{-d[H_2O_2]}{dt} = k [H_2O_2] [I^-] \quad \dots \quad (2)$$

where, k is the second order rate constant, $[]$'s represent molar concentrations of the respective species. The unit of k is $(\text{mole/lit})^{-1} \cdot (\text{time})^{-1}$.

The reaction actually occurs in two steps :



The first step is the rate-determining step.

If the iodide ion concentration, $[I^-]$, is kept constant, in large excess, the reaction becomes kinetically pseudo first order in $[H_2O_2]$. This condition is achieved by adding sodium thiosulfate solution continuously in small amounts to the reaction mixture, when thiosulfate ($S_2O_3^{2-}$) ions react with the liberated I_2 and regenerate I^- according to



Under these conditions the rate equation (2) is transformed to

$$-d[\text{H}_2\text{O}_2]/dt = k_1[\text{H}_2\text{O}_2] \quad \dots \quad (2a)$$

$$\text{where, } k_1 = k[\text{I}^\cdot] \quad \dots \quad (2b)$$

k_1 is the pseudo first order rate constant of the reaction. Integrating this equation (2a) with the boundary conditions at $t = 0$, $[\text{H}_2\text{O}_2] = a$; at $t = t$, $[\text{H}_2\text{O}_2] = (a - x)$, where, x = amount of H_2O_2 reacted \equiv equivalent of I_2 liberated \equiv equivalent of thiosulfate consumed, one obtains :

$$k_1 = \frac{2.303}{t} \log_{10} \left(\frac{a}{a-x} \right) \quad \dots \quad (2c)$$

If, V_o = titre value of thiosulfate for iodine liberated by a fixed volume, (say 10 ml) of H_2O_2 solution, this is equivalent to the initial concentration of H_2O_2 i.e., a .

V_t = titre value of the same thiosulfate solution for the iodine liberated by the same volume (10 ml) of H_2O_2 present in the reaction mixture (undergoing reaction) at time t ; this is equivalent to x

Substituting for a and $(a - x)$ in the rate equation (2c) one obtains the working equation,

$$k_1 = \frac{2.303}{t} \log \frac{V_o}{V_o - V_t} \quad \dots \quad (2d)$$

$$\therefore \log \frac{V_o}{V_o - V_t} = \frac{k_1}{2.303} \cdot t \quad \dots \quad (2e)$$

A plot of $\log [V_o/(V_o - V_t)]$ against t will be a straight line of slope $= k_1 / 2.303$ and passing through the origin. k_1 may be evaluated from the slope.

Procedure :

1. Prepare the following solutions.

- i) 50 ml of "2-vol." H_2O_2 solution, by exact dilution of "10-vol" or "20-vol" H_2O_2 .
- ii) 250 ml of KI solution (4 g. of KI/litre)
- iii) 50 ml of (1:2) H_2SO_4 solution ($\sim 12 \text{ N}$).
- iv) 250 ml of ($\sim \text{N}/20$) sodium thiosulfate solution : $\sim 3\text{-}4 \text{ g. of } \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} / 250 \text{ ml.}$

2. To 10 ml of prepared "2-vol" H_2O_2 solution, add 2 g. of KI (solid) and 10 ml of the $\sim 12(\text{N})$ H_2SO_4 solution. Keep the reaction mixture in dark for 10 minutes. Titrate the liberated iodine with the ($\sim \text{N}/20$) thiosulfate solution using starch indicator. This titre value is V_0 .
3. Take 250 ml of the prepared (4 g. lit^{-1}) KI solution in a 500 ml conical flask, add 15 ml of $\sim 12(\text{N})$ H_2SO_4 solution and 5 ml of starch indicator. Fill the burette with the prepared thiosulfate solution. Add 10 ml of the "2-vol." H_2O_2 solution into the reaction mixture using a mechanical sucking pipette and start the stop watch at the time of half discharge. Shake the reaction flask to mix uniformly. A blue colour will soon appear. Discharge the blue colour immediately by adding the ($\sim \text{N}/20$) thiosulfate solution from a burette (2-3 ml may be required). Record the time of reappearance of the blue colour and the titre of the thiosulfate solution. The volume of thiosulfate consumed will correspond to the time of reappearance of the blue colour. Continue this process till the titre values are less than 20% of V_0 . These titres constitute the V_t values.
4. Plot $\log_{10}[V_0 / (V_0 - V_t)]$ against time, t , and draw the best straight line passing through the origin and the experimental points and calculate the value of the pseudo first order rate constant, k_1 , from the slope.

Chapter – 10

Advanced Physicochemical Experiments

(a) Experiments based on Polarimetry

Introduction : When plane-polarised light is passed through an optically active substance present either as a pure liquid or in solution, the plane of polarisation of this plane-polarised light is rotated either to the left or to the right. If this rotation occurs to the right, the substance is called *dextrorotatory* and if the rotation occurs to the left then it is called *laevorotatory*.

The sign and magnitude of the angle of rotation θ (measured in degrees) depend upon; (i) temperature, (ii) wavelength of the light source used (usually monochromatic), (iii) optical path length of the sample, (iv) chemical identity of the substance (i.e., its three-dimensional structure), (v) *density* of the substance (if it is a pure liquid) or the *concentration* of the substance (in percent weight / volume, i.e. % w/v) in solution in an optically inactive solvent.

Experiment No. – 1 : To determine the specific rotation of a given optically active compound and to determine the percentage composition of its aqueous solution using a polarimeter.

Theory : The optical rotation θ of a pure liquid is expressed as :

$$\theta = [\alpha]_{\lambda}^t l d \quad \dots \quad (1)$$

where, l = path length in decimetre, d = density in g/ml and $[\alpha]_{\lambda}^t$ is the *specific rotation* of the substance at temperature $t^{\circ}\text{C}$ for the light of wavelength λ . The shorter is the wavelength, the higher is the value of $[\alpha]_{\lambda}^t$. Rearranging eqn.(1) one obtains :

$$[\alpha]_{\lambda}^t = \frac{\theta}{l d} \quad \dots \quad (2)$$

here, $\frac{1}{d}$ is the volume in ml containing 1 gm of active substance.

If C g. of an optically active substance is present in 100 ml solution in an optically inactive solvent, then 1 gram of the substance is present in $100/C$ ml. Thus,

$$[\alpha]_{\lambda}^t = \frac{\theta}{l} \left(\frac{100}{C} \right) = \frac{100 \cdot \theta}{Cl} \quad \dots \quad (3)$$

OR

$$\theta = ([\alpha]_{\lambda}^t \cdot Cl) / 100 \quad \dots \quad \dots \quad \dots \quad (4)$$

If a series of unsaturated solutions of concentrations C_i ($i = 1, 2, 3, \dots$) of an optically active substance are prepared in an optically inactive solvent and their optical rotations θ_i are measured at a fixed wavelength, λ , at a fixed temperature, using a polarimeter tube of length l dm., then the graphical plot of θ_i versus C_i will be a straight line passing through the origin (Fig. 1) and will have a slope of $[\alpha]_{\lambda}^t \cdot (l/100)$. Evaluating the slope graphically the specific rotation, $[\alpha]_{\lambda}^t$, is obtained from the relation :

$$[\alpha]_{\lambda}^t = \frac{100 \times \text{slope}}{l} \quad \dots \quad \dots \quad \dots \quad (5)$$

since l is known. For laevorotatory substances the *magnitude* of θ (in degrees) should be chosen for the ordinate (y - axis) and the sign suitably adjusted for specific rotation.

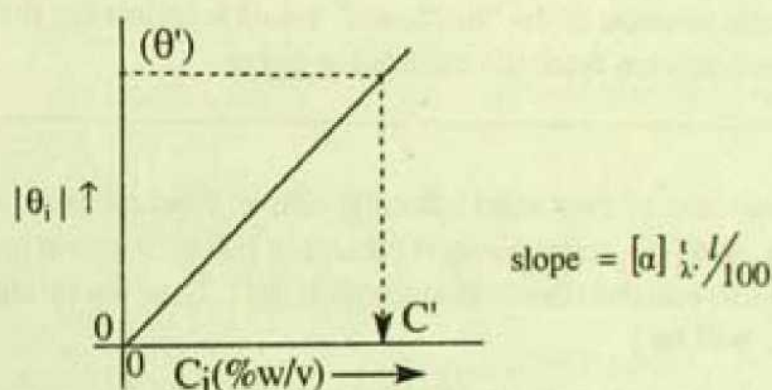


Fig. 1 : Calibration curve (angle of rotation $|\theta_i|$ absolute versus concentration C_i in % w/v)

If a solution of the same optically active substance of unknown concentration (C') gives an optical rotation (θ') under the same experimental setup at the same temperature, its concentration can be found out from this calibration curve (Fig. 1).

Procedure : (Sample : Sucrose)

1. Weigh out accurately ~ 15 g of (A.R.) sucrose (cane sugar) in a 100 ml volumetric flask, dissolve in distilled water and make up to the mark. Strength of the solution = ~ 15% (w/v).

2. Dilute 40 ml and 30 ml of this solution to 50 ml in volumetric flasks to obtain respectively 12% and 9% solutions. These solutions may be further diluted to obtain 6%, 4.5% and 3% solutions.
3. Light up the lamp of the polarimeter. Fill the polarimeter tube with distilled water. Care should be taken so that no air bubble is present in the tube.
4. Adjust the instrument to find instrumental error (if any). Record the length of polarimeter tube, in decimetre and temperature in °C and the angle of rotation for water.
5. Measure the optical rotations due to 3, 4.5, 6, 9, 12 and 15% solutions each time adjusting the angle of rotation of the analyser.
6. Find the corrected value of angle of rotation with respect to water for each concentration.
7. Plot the corrected angle of rotation versus concentration (in % w/v) on a m.m. graph paper.
8. Draw the best straight line passing through the origin and the experimental points and find its slope. Finally find the value of specific rotation at room temperature.
9. Measure the angle rotation of the "unknown" solution following the same procedure and find its concentration from the calibration curve.

Note : If m g. of a mixture of two solid optically active substances (1 and 2) of known specific rotations, $[\alpha]_1$ and $[\alpha]_2$ respectively is present in 100 ml solution in a non-interacting and optically inactive solvent, then the optical rotation, $\theta_{(1,2)}$, of the mixture, by additivity of optical rotation, will be :

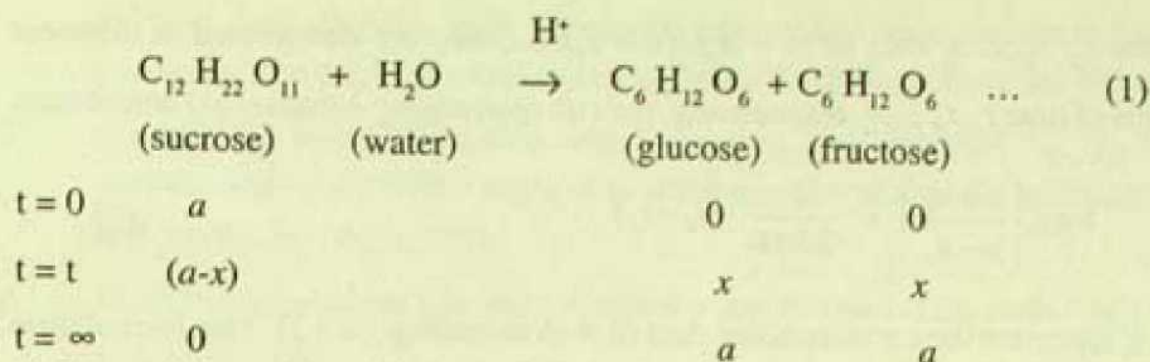
$$\theta_{(1,2)} = \theta_1 + \theta_2 = (l/100) (m_1[\alpha]_1 + m_2[\alpha]_2)$$

where, $m_1 + m_2 = m$ (known). Thus the percentage composition of the mixture can be determined.

Experiment No. – 2 : To study the kinetics of inversion of cane sugar using a polarimeter.

Theory :

Inversion of cane sugar (sucrose) takes place due to its hydrolysis in the presence of H^+ ions as catalyst in aqueous medium to produce glucose and fructose in equimolar proportion.



Since sucrose is *dextro-rotatory* (specific rotation + 66.5°) whereas the hydrolysed mixture consisting of equimolar quantities of glucose and fructose is *laevo-rotatory* (specific rotations + 52.7° and - 92.0° respectively at 25°C), an inversion in the sign of rotation of the solution occurs due to this reaction, which signifies the term, *inversion*.

The rate of the reaction (1) depends up on the concentrations of sucrose, water and hydrogen ions. Water being present in large excess, its concentration remains virtually unchanged. Concentration of the H⁺ ion also remains unchanged since it is not used up in the reaction. So, the rate of the reaction (1) is proportional to concentration of sucrose only. Thus the 'inversion' reaction (1) becomes kinetically the of *first order*. This is an example of *pseudo-unimolecular* reaction.

The rate law of the reaction may be expressed according to (2) :

$$\text{rate} = - \frac{d}{dt} [\text{sucrose}] = k [\text{sucrose}] \quad \dots \quad \dots \quad \dots \quad (2)$$

where, [] represents concentration in mol. L⁻¹, k is the first order rate constant (unit : time⁻¹). The (-) sign indicates decrease of the rate with time t.

If *a* is the initial concentration of sucrose at time, *t* = 0 and *x* is the concentration of sucrose decomposed during time *t* = *t*, then (*a* - *x*) is the concentration of sucrose remaining at *t* th. instant, then the rate equation (2) may be expressed as :

$$- \frac{d}{dt} (a-x) = k(a-x) \quad \dots \quad \dots \quad \dots \quad (3a)$$

or,

$$\frac{dx}{dt} = k(a-x) \quad \dots \quad \dots \quad \dots \quad (3)$$

On integrating one obtains :

$$\log_{10} \left(\frac{a}{a-x} \right) = \frac{kt}{2.303} \quad \dots \quad \dots \quad (4)$$

If the quantities x_1, x_2, \dots, x_n etc., or $(a - x_1), (a - x_2), \dots$ etc., are determined at different $(a - x_n)$ intervals of time t_1, t_2, \dots, t_n respectively, then on rearranging equation (4) one obtains

$$\log_{10} \left(\frac{a - x_1}{a - x_n} \right) = \frac{k}{2.303} (t_n - t_1) \quad \dots \quad (5)$$

where, t_n and x_n represent the corresponding data of n -th recording, ($n > 1$). This formulation eliminates the need for accurate determination of the initial concentration a .

If θ_0 , and θ_∞ are the corrected angles of rotation at the beginning ($t = 0$) and at the end ($t = \infty$) of the reaction, and θ_1 and θ_n be the values at times t_1 and t_n , then $(\theta_0 - \theta_\infty)$ will be proportional to the initial concentration a , $(\theta_1 - \theta_\infty)$ will be proportional to $(a - x_1)$ and $(\theta_n - \theta_\infty)$ will be proportional to $(a - x_n)$ respectively. The relation (5) is thus transformed to (5a) :

$$k = \frac{2.303}{t_n - t_1} \log_{10} \left(\frac{\theta_1 - \theta_\infty}{\theta_n - \theta_\infty} \right) \quad \dots \quad (5a)$$

Thus, k can be determined from the slope of straight line obtained by plotting logarithmic terms of eqn. 5(a) against time interval $(t_n - t_1)$.

Since the strong acid (the catalyst) is completely dissociated at the concentration employed, the rate constants (k_I and k_{II}) of the reaction with two sets of concentrations of the strong acid are directly proportional to their concentrations $[\text{acid}]_I$ and $[\text{acid}]_{II}$

$$\frac{k_I}{k_{II}} = \frac{[\text{acid}]_I}{[\text{acid}]_{II}} \quad \dots \quad (6)$$

Thus, the ratio of the two concentrations of the strong acid can be evaluated from ratio of the rate constants of the reaction at the two concentrations.

Procedure :

1. Prepare 25% (w/v) solution of cane sugar by weighing ~ 25 g. of the sugar and dissolving the same in 100 ml of water in a volumetric flask.
2. Prepare 100 ml of ~ (N) HCl solution and 50 ml of ~ (N/2) HCl solution by exact dilution of the ~ (N) HCl solution. Record the temperature of the experiment.
3. Take 25 ml of the sugar solution in a dry conical flask. To it add 25 ml of the ~ (N) HCl solution and start the stopwatch at the time of half-discharge of the acid solution. Mix uniformly.

4. Fill the polarimeter tube with the reaction mixture and place the tube in the polarimeter and record the angle of rotation and the time. Keep away from the light source.
5. Measure the angle of rotation with increasing time intervals, i.e., 2, 5, 10, 15, 25 minutes and so on till the angle of rotation remains practically unchanged with time and record the (θ_n, t_n) data.
6. Wash the polarimeter tube with distilled water and repeat the steps 3 to 5 with the (N/2) HCl solution.
7. For the determination of the angles of rotation (θ_∞) at infinite time, digest the remaining parts of the two reaction mixtures at $\sim 60^\circ\text{C}$ in a water bath for about 45 minutes cool to room temperature and measure the angles of rotation as before.
8. Plot $\log \left(\frac{\theta_1 - \theta_\infty}{\theta_n - \theta_\infty} \right)$ versus $(t_n - t_1)$ and find the rate constants $(k_1 \text{ and } k_{II})$ of the reaction at the two concentration (1N) and (N/2)) of the HCl solutions, and hence find k_I/k_{II} .

Note : The relation (5a) may be derived as follows :

Let the initial concentration of sucrose be a moles in a volume V ml of reaction mixture (V remains constant throughout the reaction); M_S, M_G, M_F represent the molar masses of sucrose (S), glucose (G) and fructose (F); $\alpha_S, \alpha_G, \alpha_F$ be the corresponding specific rotations at the experimental temperature and wavelength of plane-polarised light used. Let $\theta_0, \theta_t, \theta_n$ and θ_∞ represent the specific rotations (in degrees) of the reaction mixture at times $t = 0, t = t_1, t = t_n$ and $t = \infty$ (i.e., end of reaction) respectively when placed in a polarimeter tube of l decimetres in length. As the optical rotation is an additive property,

$$\text{at } t = 0, \quad \theta_0 = (\alpha_S \cdot M_S) \left(\frac{l}{V} \right) a \quad \dots \dots (7)$$

$$\text{at } t = t \quad \theta_t = [\alpha_S \cdot M_S(a - x_t) + (\alpha_G \cdot M_G + \alpha_F \cdot M_F) x_t] \frac{l}{V} \quad \dots \dots (8)$$

$$\text{at } t = \infty, \quad \theta_\infty = (\alpha_G \cdot M_G + \alpha_F \cdot M_F) \frac{l}{V} a \quad \dots \dots (9)$$

$$\text{Thus,} \quad \theta_0 - \theta_\infty = \frac{l}{V} \cdot [\alpha_S \cdot M_S - \alpha_G \cdot M_G - \alpha_F \cdot M_F] (a) \quad \dots \dots (10)$$

$$\theta_t - \theta_\infty = \frac{l}{V} \cdot [\alpha_S \cdot M_S - \alpha_G \cdot M_G - \alpha_F \cdot M_F] (a - x_t) \quad \dots \dots (11)$$

$$\frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty} = \frac{a}{a - x_t} \quad \dots \dots (12)$$

$$\therefore \frac{\theta_1 - \theta_{\infty}}{\theta_n - \theta_{\infty}} = \frac{a - x_1}{a - x_n} \quad \dots \quad (13)$$

(b) Experiments based on conductometry

Introduction :

When the solution of an electrolyte is placed between the electrodes in a conductivity cell, the conductance (G) of the solution is given by

$$G = k (l/a)^{-1}$$

where, k (kappa) is the specific conductance of the electrolyte solution, (l/a) is the *cell constant*, where, l is the distance in cm between the two electrodes and a is their surface area in cm^2 . The unit of G is ohm^{-1} , (mho, Siemens), and the unit of k (kappa) is $\text{ohm}^{-1} \cdot \text{cm}^{-1}$. k is numerically equal to the conductance of the electrolyte contained in a cube of 1 cm edge. The equivalent conductance (Λ) of an electrolyte is numerically equal to the conductance of one gram equivalent of the electrolyte placed between two parallel electrodes of infinite dimension situated 1 cm. apart from one another. Equivalent conductance (Λ) is related to specific conductance (k) according to the relation :

$$\Lambda = 1000 k/c$$

where, c , is the number of gram equivalents of the electrolyte dissolved in 1000 cm^3 (i.e., one litre) of the solution. Thus, unit of Λ is $\text{ohm}^{-1} \cdot \text{cm}^2 \cdot \text{g-equiv}^{-1}$. Since $1000/c$ is the volume, in cm^3 , containing 1 gram equivalent of the electrolyte, Λ is numerically equal to the conductance of 1 gram equivalent of the electrolyte, whose volume is $V \text{ cm}^3$, placed between two parallel electrodes each of area $V \text{ cm}^2$ and situated 1 cm apart from one another.

Effect of dilution on k and Λ : The specific conductance, k , is proportional to the concentrations of the ions present and to their mobilities (i.e., speed under unit potential gradient). On the other hand equivalent conductance, Λ , is proportional to the total number of ions furnished by one gram equivalent of the electrolyte and their respective mobilities. Strong electrolytes are ~100% dissociated at almost all concentrations. Dilution reduces the concentration of number of ions but not the total number of ions in one gram equivalent of the electrolyte. Mobility of the ions are increased slightly on dilution because of the reduction in forces of inter-ionic attraction. Thus, k , decreases sharply but Λ shows a slight increase on dilution. At infinite dilution, Λ reaches a limiting value, Λ_{∞} , called *equivalent conductance at infinite dilution*. Weak electrolytes are only partially ionised in solution.

Dilution with solvent brings about a marked increase in the degree of dissociation. On dilution, concentrations of the ions definitely decrease, but the total number of ions furnished by 1 gram equivalent of the weak electrolyte increase. The speeds of the ions also increase on dilution, albeit slightly, because of the reduction in forces of inter-ionic attraction. The end result is that : k decreases, but Λ increases on dilution. As such, Λ does not reach a limiting value.

Experiment No. 3 : To determine the concentrations of each of HCl and CH_3COOH in a mixture conductometrically using standardised caustic soda solution.

Theory :

The specific conductance, k , (κ) of an electrolytic solution depends upon the concentration of the electrolyte, charges of the ions and their mobilities and may be expressed as :

$$k = \text{constant} \times \sum_i c_i u_i \quad \dots \quad (1)$$

where, c_i is the concentration of the i -th ion in g-ion/litre, and u_i is its mobility. The constant includes the absolute values of charges. Thus, for a solution of HCl in water,

$$k = \text{constant} \cdot [c_{\text{H}^+} \cdot u_{\text{H}^+} + c_{\text{Cl}^-} \cdot u_{\text{Cl}^-}] \quad \dots \quad (2)$$

since water is practically unionised. Since $c_{\text{H}^+} = c_{\text{Cl}^-} = c_{\text{HCl}}$

$$k = \text{constant} \cdot c_{\text{HCl}} [u_{\text{H}^+} + u_{\text{Cl}^-}] \quad \dots \quad (3)$$

As the strong acids are completely ionised, the initial conductance of a mixture of HCl (strong acid) and CH_3COOH (weak acid) will be entirely due to the strong acid, since the ionisation of the weak acid will be suppressed due to common-ion effect of H^+ ions. As the mobilities of H^+ , Na^+ , OH^- and CH_3COO^- ions are in the order : $\text{H}^+ > \text{OH}^- \gg \text{Na}^+ > \text{CH}_3\text{COO}^-$, in the absence of any base, the specific conductance of a mixture of HCl and CH_3COOH will be given by eqn. (3). When a small amount (x mol) of the strong base (NaOH) is added, the highly conducting H^+ ions of the completely ionised strong acid are replaced by Na^+ ions having much lower conductance. As a result, the conductance of the solution decreases, since the H^+ ion and OH^- ion combine to form unionised H_2O molecules ($\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$). Specific conductance (k') of such a mixture of strong acid (HCl), its salt (NaCl) and weak acid (CH_3COOH) will be given by :

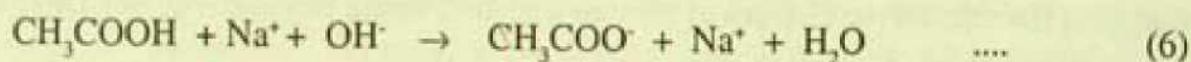
$$k' = \text{constant} [(c_{\text{HCl}} - x) \cdot u_{\text{H}^+} + c_{\text{HCl}} \cdot u_{\text{Cl}^-} + x \cdot u_{\text{Na}^+}]$$

$$= \text{constant} [c_{\text{HCl}} (u_{\text{H}^+} + u_{\text{Cl}^-}) - x (u_{\text{H}^+} - u_{\text{Na}^+})] \quad \dots \quad (4)$$

$$\therefore k' = k - \text{constant} \cdot x (u_{\text{H}^+} - u_{\text{Na}^+}) \quad \dots \quad (5)$$

Since, $u_{\text{H}^+} \gg u_{\text{Na}^+}$, so, $(u_{\text{H}^+} - u_{\text{Na}^+})$ is positive. Therefore, the plot of k' vs. x will be a straight line (AB) with negative slope (Fig. 1).

When neutralisation of the strong acid is just complete, conductance of the mixture is at its minimum (k_b) and on further addition of NaOH, neutralisation of the weak acid starts, producing the fully ionised salt, sodium acetate, $\text{CH}_3\text{COO}^-\text{Na}^+$ and unionised H_2O molecules as before :



If y mol of the strong base (Na^+OH^-) is added after complete neutralization of HCl, then the specific conductance, k' , will be given by

$$k' = k_b + \text{constant} \cdot y \cdot (u_{\text{Na}^+} + u_{\text{CH}_3\text{COO}^-}) \quad \dots \quad (7)$$

which indicates the plot of k' vs. moles of NaOH (y) will be a straight line (BC) with positive slope (Fig. 1).

Owing to the common ion effect by the CH_3COO^- ion, the ionisation equilibrium ($\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$) of acetic acid is repressed to some extent, as a result, conductance of the solution falls slightly, but soon increases, as the conducting power of the highly ionised salt, $\text{CH}_3\text{COO}^-\text{Na}^+$, exceeds that of the weak acid (CH_3COOH) which it replaces.

Immediately after the equivalence point, C, conductance (k_c) of the solution shows a steep rise (Fig. 1), as the conducting power of OH^- ions from the excess NaOH is much higher than that of acetate ions. If z mol of the base is added after complete neutralization of the two acids, HCl and CH_3COOH , the solution will contain Na^+ , CH_3COO^- , Cl^- and OH^-

ions. Specific conductance (k') of such a solution may be expressed according to,

$$k' = k_c + \text{constant} \cdot z \cdot (u_{\text{Na}^+} + u_{\text{OH}^-}) \quad \dots \quad (8)$$

which indicates the plot of k' vs. mols of NaOH (z) will be a straight line (CD) with positive slope (Fig. 1). Since $u_{\text{OH}^-} \gg u_{\text{CH}_3\text{COO}^-}$, the slope of the straight line (CD) will be higher than that of the straight line (BC).

Volume change during the titration will be almost negligible if the concentration of the titrant (NaOH) is 10 times as the concentration of the acids. Under this condition the plot of specific conductance (k') vs. volume (V) of titrant (NaOH) for a particular neutralization will be practically a straight line (Fig. 1). The resulting plot will consist of straight lines mutually intersecting at the equivalent points. If the titre V_1 of NaOH corresponds to the first neutralization point, i.e., of the strong acid (HCl), and the titre V_2 corresponds to the second neutralization point i.e., of the total quantity of strong acid and weak acid, then, $(V_2 - V_1)$ ml of NaOH is required to neutralize the weak acid (CH_3COOH) only.

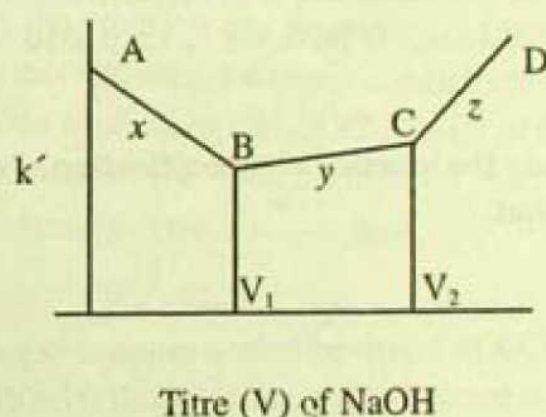


Fig. 1. Conductometric titration curve

Procedure :

1. Prepare approximately ($\sim N/2$) NaOH solution and standardize the same with standard ($N/20$) oxalic acid solution using phenolphthalein indicator. For this purpose, pipette out 10 ml of the ($\sim N/2$) NaOH into a 100 ml volumetric flask, make up to the mark with distilled water and mix uniformly. Use this diluted ($\sim N/20$) solution of NaOH as the titrant for the titration of 10 ml of standard ($N/20$) oxalic acid solution and hence calculate the exact strength of the ($\sim N/2$) NaOH solution.
2. Take 10 ml of the mixed acid solution (total acid strength $\sim N/10$) in a 100 ml beaker.

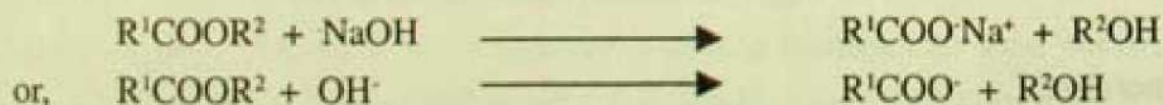
3. Dip the conductivity cell into the solution and add just sufficient amount of distilled water to cover the electrodes of the cell with solution.
4. Stir the solution and measure its conductance.
5. Add 2-4 drops of the standardized ($\sim N/2$) NaOH solution from a 10 ml burette, stir thoroughly and measure the conductance. Continue this process and each time record the number of drops of ($\sim N/2$) NaOH added and the conductance of the solution after each addition in a tabular form.
6. Plot the conductance against number of drops of ($\sim N/2$) NaOH and draw the best straight lines through the experimental points and find the points of intersections.
7. Count the number of drops of alkali that is equivalent to 1 ml of the NaOH solution. Using this, calculate the volumes of NaOH (V_1 and V_2) required for neutralization of HCl and (HCl + CH_3COOH) mixture.
8. Finally calculate the concentrations of HCl and CH_3COOH .

Note : The ionic mobilities at 25°C are as follows : H^+ (36.2), Na^+ (5.19); OH^- (20.5); CH_3COO^- (4.24) in units of $1 \times 10^{-4} (\text{cm} \cdot \text{s}^{-1}) / (\text{volt} \cdot \text{cm}^{-1})$, i.e. $1 \times 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{volt}^{-1}$.

Experiment No. 4 : To study the kinetics of saponification of ester by conductometric method.

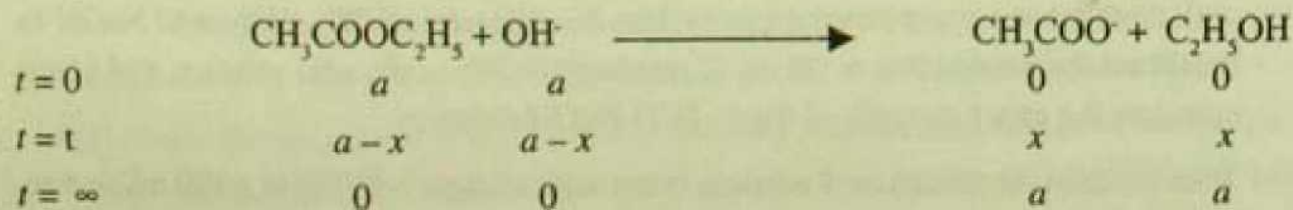
Theory :

When an ester, R^1COOR^2 , derived from a monocarboxylic acid, R^1COOH , and a monohydric alcohol, R^2OH , is treated with a caustic alkali (NaOH), the ester is hydrolysed to produce the alcohol and sodium salt of the acid :



Such alkaline hydrolysis of an ester is called *saponification*.

Ethyl acetate ($\text{CH}_3\text{COOC}_2\text{H}_5$) on alkaline hydrolysis produces ethanol ($\text{C}_2\text{H}_5\text{OH}$) and acetate (CH_3COO^-) :



The overall reaction is kinetically of second order, being first order with respect to each of the reactants, the ester and hydroxyl ions (OH^-). The rate of the overall reaction may be expressed according to (1)

$$\text{rate} = - \frac{d[\text{ester}]}{dt} = k [\text{ester}] [\text{OH}^-] \quad \dots \quad \dots \quad \dots \quad (1)$$

where, k is the rate constant in $\text{mole}^{-1} \cdot \text{litre} \cdot \text{second}^{-1}$ and $[\]$'s stand for concentrations in moles/litre. If the initial concentrations (i.e., at time $t = 0$) of both ester and alkali be a moles/litre, and those after time t be $(a - x)$, where, x is the amount of alkali / ester consumed, then,

$$\frac{dx}{dt} = k(a - x)^2 \quad \dots \quad \dots \quad (2)$$

Integration of equation (2), for $x = 0$, when, $t = 0$ yields.

$$k = \frac{1}{at} \cdot \frac{x}{a - x} \quad \dots \quad \dots \quad (3)$$

The progress of the reaction can be monitored by measuring the electrolytic conductance of the reaction mixture, since the highly conducting OH^- ions ($\lambda_0 = 198.5 \text{ ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$) are replaced by weakly conducting CH_3COO^- ions ($\lambda_0 = 40.9 \text{ ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$). If C_0 , C_t and C_∞ be the conductances of the reaction mixture at the times $t = 0$, t , and at the completion of the reaction (infinite time, $t = \infty$), then,

$$a \propto (C_0 - C_\infty) \quad \dots \quad \dots \quad \dots \quad 4(a)$$

$$x \propto (C_0 - C_t) \quad \dots \quad \dots \quad \dots \quad 4(b)$$

$$(a - x) \propto (C_t - C_\infty) \quad \dots \quad \dots \quad \dots \quad 4(c)$$

Equation (3) is then transformed to :

$$\frac{(C_0 - C_t)}{(C_t - C_\infty)} = k a \cdot t \quad \dots \quad \dots \quad \dots \quad (5)$$

A plot of $[(C_0 - C_t) / (C_t - C_\infty)]$ versus t will be a straight line passing through the origin and possessing a positive slope $= ka$. Thus, k may be evaluated from the relation,

$$k = \text{slope} / a, \quad \dots \quad \dots \quad \dots \quad (6)$$

since a is known. Here, a is calculated by diluting a known amount of the ester to a definite volume with water. C_∞ may be indirectly determined by measuring the conductance of a solution of sodium acetate, $\text{CH}_3\text{COO}^- \text{Na}^+$, of the same concentration, a , i.e., exactly equal to

the initial concentration, a , of the ester and the alkali (NaOH). The conductances C_0 , C_t and C_∞ of the reaction mixture are measured at times $t = 0$, t and ∞ respectively.

Procedure :

1. Prepare 100 ml of standard (N/20) oxalic acid solution by accurate weighing.
2. Prepare ~ 250 ml of (~N/20) NaOH solution and standardise the same against standard (N/20) oxalic acid using phenolphthalein indicator. Prepare 250 ml of exact (N/50) NaOH solution by accurate dilution of the standard (~ N/20) NaOH solution in a 250 ml volumetric flask.
3. Prepare 250 ml of (~N/20) acetic acid and standardise the same against standard (~N/20) NaOH solution using phenolphthalein indicator. Prepare 250 ml of exact (N/50) acetic acid solution by accurate dilution of the standard (~ N/20) solution.
4. Prepare an exact (N/100)NaOH solution by accurate dilution of standard (N/50) NaOH with water in a volumetric flask, and measure its conductance (C_0).
5. Prepare an exact (N/100) solution of sodium acetate, $\text{CH}_3\text{COO}^-\text{Na}^+$, by mixing equal volumes of (N/50) CH_3COOH and (N/50)NaOH solutions. Measure the conductance of this solution (C_∞).
6. Prepare a standard (N/20) ethyl acetate solution by accurate dilution. Find the amount in g. of the ester required for 250 ml of (N/20) solution. Using the relation, density = mass/volume, calculate the volume of the liquid ester required for 250 ml of (N/20) solution. Transfer the required volume of the pure ester into a 250 ml volumetric flask, make up to the mark with distilled water and mix uniformly. Prepare an exact (N/50) ethyl acetate solution by exact dilution of the prepared standard (N/20) solution.
7. In a dry 100 ml beaker, take 25 ml of (N/50) ethyl acetate, and add 25 ml of (N/50) NaOH to it from a pipette and note the time of half-discharge. Measure the conductance (C_t) of the reaction mixture at different time intervals, approximately 2, 5, 10, 15, 25, 40 minutes till the conductance remains practically unchanged with time. Record the conductance vs. time data in a tabular form. Record the temperature of the experiment.
8. Plot $(C_0 - C_t) / (C_t - C_\infty)$ against t to obtain rate constant, k , from the slope and the initial concentration, a . ($= \text{N}/100$) of the ester.

Note :

Initially (at $t = 0$) the mixture contained a mol of NaOH as the only electrolyte, specific conductance (k_0) of such a solution is given by :

$$k_0 = \text{constant. } a(u_{\text{Na}^+} + u_{\text{OH}^-}) \quad \dots \quad \dots \quad \dots \quad (7)$$

when u 's stand for ionic mobilities of the respective ions. At time t , the concentration of alkali is reduced to $(a - x)$ and the concentration of $\text{CH}_3\text{COO}^-\text{Na}^+$ produced is x . Specific conductance (k_t) of such a solution is given by :

$$\begin{aligned} k_t &= \text{Constant } [(a - x)(u_{\text{Na}^+} + u_{\text{OH}^-}) + x(u_{\text{Na}^+} + u_{\text{CH}_3\text{COO}^-})] \\ &= k_0 - \text{constant. } x. (u_{\text{OH}^-} - u_{\text{CH}_3\text{COO}^-}) \quad \dots \quad \dots \quad (8) \end{aligned}$$

Therefore, the change in specific conductance, $k_0 - k_t$, due to ester hydrolysis will be given by :

$$(k_0 - k_t) = \text{constant. } x.(u_{\text{OH}^-} - u_{\text{CH}_3\text{COO}^-}) \quad \dots \quad \dots \quad (9)$$

Similarly at the end of the reaction ($t = \infty$), the reaction mixture will contain a moles of the electrolyte, $\text{CH}_3\text{COO}^-\text{Na}^+$, and the specific conductance k_∞ of the solution will be,

$$k_\infty = \text{constant } a.(u_{\text{Na}^+} + u_{\text{CH}_3\text{COO}^-}) \quad \dots \quad \dots \quad \dots \quad (10)$$

which may be rearranged to,

$$k_\infty = k_0 - \text{constant } a. (u_{\text{OH}^-} - u_{\text{CH}_3\text{COO}^-}) \quad \dots \quad \dots \quad \dots \quad (11)$$

$$\text{Consequently, } k_0 - k_\infty = \text{constant } a.(u_{\text{OH}^-} - u_{\text{CH}_3\text{COO}^-}) \quad \dots \quad \dots \quad (12)$$

From (8) and (11) one obtains

$$k_t - k_\infty = \text{constant } (a - x). (u_{\text{OH}^-} - u_{\text{CH}_3\text{COO}^-}) \quad \dots \quad \dots \quad (13)$$

$$\text{Hence, } \frac{k_0 - k_t}{k_t - k_\infty} = \frac{x}{a - x} \quad \dots \quad \dots \quad (14)$$

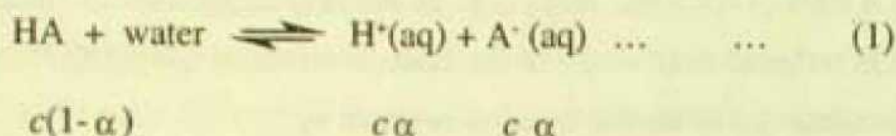
For a cell with fixed cell constant, specific conductance (k) is proportional to the conductance (C) of the solution.

$$\text{Hence } \frac{C_0 - C_t}{C_t - C_\infty} = \frac{k_0 - k_t}{k_t - k_\infty} = \frac{x}{a - x} \quad \dots \quad \dots \quad (15)$$

Experiment No. 5(a) : To determine the ionisation constant of a weak acid by conductometric method.

Theory :

A monobasic weak acid, HA, is partially ionised in aqueous solution. The degree of ionisation (α) at any temperature increases with dilution :



The degree of ionisation (α), at a particular concentration (c) of the weak electrolyte, HA, may be well approximated by the ratio, Λ / Λ_∞ , where, Λ is the equivalent conductance of HA at concentration c and Λ_∞ is its equivalent conductance at infinite dilution. Ionisation constant (K_a) of the weak acid, HA, may be defined according to,

$$K_a = \frac{a_{\text{H}^+} \cdot a_{\text{A}^-}}{a_{\text{HA}}} \quad \dots \quad \dots \quad \dots \quad (2)$$

where, a 's stand for the activities of the respective species. Since, $a = f \cdot c$, where, f is the ionic activity coefficient and c is the molar concentration, eqn. (2) may be transformed to :

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \cdot \frac{f_{\text{H}^+} \cdot f_{\text{A}^-}}{f_{\text{HA}}} \quad \dots \quad \dots \quad \dots \quad (3)$$

where, $[]$'s represent concentrations c in g-mole / litre or g-ion / litre. For a dilute solution of weak acid, the ionic strength of the medium will be very low, and the numerical value of the activity coefficients f 's are very close to unity (*Debye-Huckel limiting law*). Under this condition the eqn. (3), according to *Ostwald's dilution law*, may be written as :

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad \dots \quad \dots \quad (3a)$$

$$= c\alpha \cdot c\alpha / c(1-\alpha)$$

$$= c\alpha^2 / (1-\alpha) \quad \dots \quad \dots \quad (3b)$$

Substituting $\alpha = \Lambda / \Lambda_\infty$, one obtains from eqn. (3b),

$$K_a = \frac{c(\Lambda/\Lambda_\infty)^2}{1-\Lambda/\Lambda_\infty} \quad \dots \quad \dots \quad (4)$$

which on rearrangement yields,

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_0} + \left(\frac{1}{K_a \cdot \Lambda_0^2} \right) \cdot \Lambda c \quad \dots \quad \dots \quad \dots \quad (5)$$

If a series of solutions of the weak acid (HA) of different concentrations are prepared and their equivalent conductances are determined by measuring their specific conductances in a cell of known cell constant, then by plotting $\frac{1}{\Lambda}$ (y-axis) against Λc (x-axis), one may

obtain a straight line with a positive intercept of $\frac{1}{\Lambda_0}$ and a positive slope of

$\left(\frac{1}{K_a \cdot \Lambda_0^2} \right)$. Thus, K_a may be calculated using the relation :

$$K_a = \frac{(\text{intercept})^2}{\text{slope}} \quad \dots \quad \dots \quad (6)$$

provided Λ_0 is determined with sufficient accuracy. Therefore, by this method, the ionisation constant (K_a) and as well as the equivalent conductance at infinite dilution (Λ_0) of a weak electrolyte (HA) can be determined.

Procedure :

1. Prepare 250 ml a standard KCl solution (strength slightly higher than N/10) in *conductivity water*. Prepare 100 ml an exact (N/10) KCl solution by accurate weighing and 100 ml of an exact (N/100) KCl solution by accurately diluting the prepared standard (N/10) KCl solution with conductivity water.
2. Rinse a 100 ml beaker and the conductivity cell with the exact (N/100) KCl solution thoroughly and then pour sufficient volume of this solution into the beaker so that the electrodes of the cell are completely immersed in the solution. Record the conductance. Repeat this procedure with the exact (N/10) KCl solution. Calculate the *mean cell constant* from the measured conductance values of these two solutions, using the literature values of the specific conductance of KCl solutions at these concentrations at the same temperature.
3. Prepare 100 ml of a standard (N/20) acetic acid solution. Prepare 100 ml of an exact (N/50) acetic acid solution by accurate dilution of the standard (N/20) solution with conductivity water.

4. In a clean, dry 100 ml beaker take 50 ml of the (N/50) acetic acid solution using a 25 ml pipette. Dip the clean, dry conductivity cell into this solution, stir well and record the conductance. Carefully pipette out 25 ml of (N/50) acetic acid solution and pour in exactly 25 ml conductivity water into the cell using the same pipette after washing it properly. Mix the solution well and record the conductance of this (N/100) acetic acid solution as before. Follow the same procedure to obtain (N/200), (N/400) and (N/800) acetic acid solutions and record their conductances following the same procedure.
5. Calculate the equivalent conductance values of all the acetic acid solutions using the mean value of the cell constant with the aid of the relation ::

$$\Lambda = \frac{1000k}{c}$$

1. Plot $(1/\Lambda)$ versus Λc and find Λ_0 from the intercept, and then K_a from the slope and intercept using the solution (6).

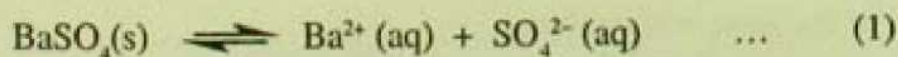
Note : Compare the experimental value of Λ_0 obtained from the intercept with the calculated value of Λ_0 of acetic acid using the known conductance values for hydrogen ion and acetate ion with proper temperature correction. [$\lambda_{H^+} = 349.82$ and $\lambda_{CH_3COO^-} = 40.9$ ohm⁻¹.cm²/g-equivalent at 25°C at infinite dilution].

Experiment No. 5(b) : To determine the solubility and solubility product of a sparingly soluble salt by conductometric method.

Theory :

The *solubility* of a solute in a solvent at a particular temperature is defined as the number of grams of the solute that dissolves in 100 grams of the solvent to produce a saturated solution. Solubility is more conveniently expressed in molar concentration i.e., number of moles of solute present in 1 litre of saturated solution at a particular temperature.

In a saturated solution in water, a *sparingly soluble salt* such as, BaSO₄ ionises as,



The equilibrium constant, or, the *solubility product*, K_{sp} , is given by

$$K_{sp} = a_{Ba^{2+}} \times a_{SO_4^{2-}} \quad \dots \quad (1a)$$

where, a 's represent the activities of the respective ionic species. For a sparingly soluble salt like BaSO_4 , the concentrations of the ions are very small. So, the activities may be replaced by concentrations (c) of the respective ions. If, S moles/litre be the concentration of BaSO_4 in solution at a particular temperature, then K_{sp} will be given by

$$K_{sp} = c_{\text{Ba}^{2+}} \times c_{\text{SO}_4^{2-}} = S^2 \quad \dots \quad (2)$$

The specific conductance κ (kappa) of a solution of an electrolyte depends upon the concentrations and mobilities of the ions. The conductance (G) of a solution is given by

$$G = \kappa \times (l/a) \quad \dots \quad (3)$$

where, l = distance between the two electrodes in cm and a = area of cross section of the electrodes in cm^2 , (l/a) is the cell constant. The equivalent conductance, Λ , is given by :

$$\Lambda = 1000 \kappa / c \quad \dots \quad (4)$$

where, c , is the concentration of the electrolyte in g. eqv./litre.

Since, S = concentration of BaSO_4 in moles/litre, then,

$$c = 2S \quad \dots \quad (5)$$

The solution of BaSO_4 being very dilute, the Λ can be calculated using the relation,

$$\begin{aligned} \Lambda &\equiv \Lambda_\infty \text{ (at infinite dilution)} \\ &= \lambda_\infty^+ + \lambda_\infty^- \text{ (by Kohlraush's law)} \quad \dots \quad (6) \end{aligned}$$

$$\text{and } \kappa \text{ (for } \text{BaSO}_4 \text{ solution)} = \kappa \text{ (solution)} - \kappa \text{ (water)} \quad \dots \quad (7)$$

From the standard ion-conductance data at infinite dilution at the experimental temperature, Λ_∞ and hence Λ can be calculated from (6). S and hence K_{sp} can be evaluated from eqns. (5) and (2) after calculating κ (BaSO_4 solution) using equation (7).

Notes :

- The expressions (1) and (2) for 1-2, 1-3, 2-3 types of electrolytes should be modified accordingly.
- In case of AgCl the equation (5) will be, $c = S$.
- Ion conductances (λ_∞) of Ag^+ , Cl^- , $\frac{1}{2} \text{Ba}^{2+}$, $\frac{1}{2} \text{SO}_4^{2-}$ are 64, 79, 66, 83 $\text{ohm}^{-1} \cdot \text{cm}^2/\text{g}$. equivalent respectively at 25°C .

Procedure :

- Record the room temperature. Use conductivity water of uniform quality and known specific conductance, κ (water), exclusively for this experiment.
- Prepare exactly 0.1 (N) and 0.01 (N) KCl solutions by accurate weighing and proper dilution.

- (3) Measure the conductance of these two solutions (2) using the same conductance cell. Find the specific conductances of 0.1(N) and 0.01(N) KCl solutions at room temperature from literature and estimate the mean cell constant (l/a).
- (4) Prepare a saturated solution of the sparingly soluble salt in conductivity water and measure its conductance using the same conductance cell as before.
- (5) Measure κ (solution). Subtract from it κ (water) to obtain κ (electrolyte).
- (6) Note the values of the equivalent ionic conductances $\lambda_o^{(+)}$ and $\lambda_o^{(-)}$ (for the cation and anion respectively from literature) and find Λ_o using the eqn. $\Lambda_o = \lambda_o^{(+)} + \lambda_o^{(-)}$.
- (7) Calculate c (solubility in g. equiv. per litre) using equation (4) and obtain S (solubility in moles per litre) using eqn. (5).
- (8) Calculate K_{sp} using the relation (2).

(c) Experiments based on potentiometry

Introduction :

For a redox system,



occurring at a neutral electrode, the electrode potential (reduction potential) E , in volts, at a particular temperature, T Kelvin, is given by the *Nernst equation* :

$$E = E^\circ + \frac{RT}{nF} \ln \frac{a_{\text{Ox}}}{a_{\text{Red}}} \quad \dots \quad \dots \quad \dots \quad (2)$$

where, E° is the standard reduction potential, n is the number of electron change in the redox process (1), a_{Ox} and a_{Red} represent the activities of the oxidant and reductant respectively, R is the universal gas constant and F is the Faraday constant. The standard electrode potential (E°) is the value of the electrode potential (E) when all the species involved in the redox reaction (1) are present at their standard states of unit activity.

Since, activity (a) = molar concentration (c) \times activity coefficient (f), the eqn. (2) may be written as,

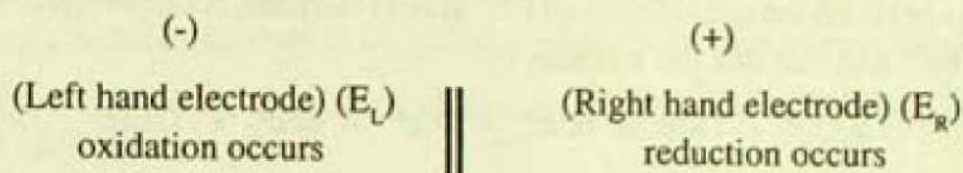
$$E = E^\circ + \frac{RT}{nF} \ln \frac{C_{\text{Ox}} \cdot f_{\text{Ox}}}{C_{\text{Red}} \cdot f_{\text{Red}}} \quad \dots \quad \dots \quad \dots \quad (3)$$

When the solution is dilute, the ionic strength is low, the value of the activity coefficients (f) approach unity and the concentrations (c) approach activities (a). Substituting the values of R, and F, and expressing the logarithmic term to base 10, (\log_{10}), the eqn. (3) of the electrode potential (E) at 25°C (i.e., 298 K) may be expressed according to,

$$E = E^\circ + \frac{0.059}{n} \log_{10} \frac{[\text{Ox}]}{[\text{Red}]} \quad \dots \quad (4)$$

where, []'s represent concentrations (c) of the respective species.

When two different redox electrodes are electrochemically connected an electrochemical cell is formed which is conventionally represented as :



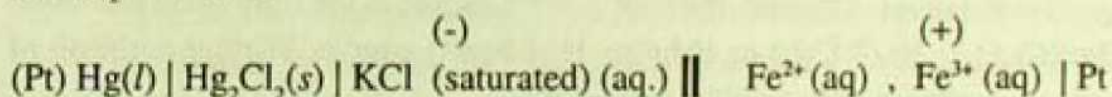
Electromotive force (e.m.f.) of this cell (E_{cell}) is the difference between the redox potentials of the right hand and left hand electrodes :

$$E_{\text{cell}} = E_R - E_L \quad \dots \quad (5)$$

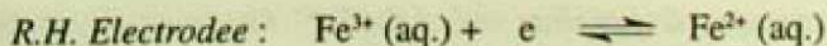
Experiment – 6 : To titrate potentiometrically the given ferrous ammonium sulphate solution using $\text{K}_2\text{Cr}_2\text{O}_7$ / KMnO_4 as standard and hence to find the redox potential of the $\text{Fe}^{3+} / \text{Fe}^{2+}$ system on the hydrogen scale.

Theory :

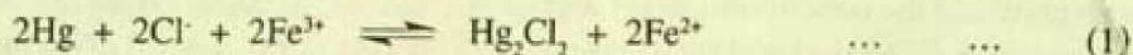
When the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox system is coupled with a saturated calomel electrode (SCE), $\text{KCl (satd.) Hg}_2\text{Cl}_2(s) \text{ Hg (l)}$ as the reference electrode, the following electrochemical cell is produced :



where, the symbol, \parallel , stands for agar – KCl salt-bridge which eliminates the liquid junction potential. The half-cell reactions at the electrodes are :



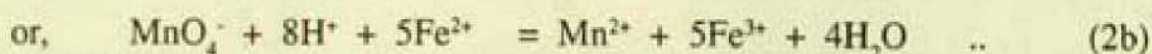
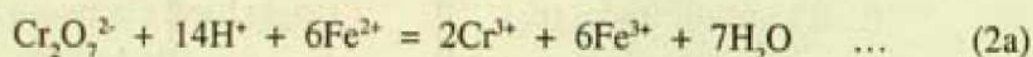
Overall cell reaction is :



and the e.m.f. of the cell (E_{cell}) is given by,

$$\begin{aligned}
 E_{\text{cell}} &= E_R - E_L = E_{\text{Fe}^{3+}/\text{Fe}^{2+}} - E_{\text{SCE}} \\
 &= E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} + 0.059 \log \left(\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \right) - E_{\text{SCE}} \quad (\text{at } 25^{\circ}\text{C}) \quad \dots \quad (1a)
 \end{aligned}$$

Since E_{SCE} remains unchanged, if the temperature remains unchanged, the e.m.f. of the cell (E_{cell}) varies with variation of the ratio, $[\text{Fe}^{3+}] / [\text{Fe}^{2+}]$. If an oxidant ($\text{K}_2\text{Cr}_2\text{O}_7$ or KMnO_4 as the case may be) is added to a solution of Fe^{2+} in acid medium, concentration of Fe^{2+} will fall and that of Fe^{3+} will rise due the reaction :



as the case may be. With progressive addition of the oxidant, the ratio ($[\text{Fe}^{3+}] / [\text{Fe}^{2+}]$) progressively increases, consequently E_{cell} increases. At the half-equivalence point, exactly half of the Fe^{2+} originally present is converted to Fe^{3+} , and the ratio ($[\text{Fe}^{3+}] / [\text{Fe}^{2+}]$) becomes unity. At this point,

$$E_{\text{cell}} = E_{\frac{1}{2}} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} - E_{\text{SCE}} \quad \dots \quad (3)$$

$$\therefore E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} = E_{\frac{1}{2}} + E_{\text{SCE}} \quad \dots \quad (4)$$

E_{SCE} is obtainable from literature. Thus, $E^{\circ} (\text{Fe}^{3+} / \text{Fe}^{2+})$ at room temperature may be obtained if $E_{\frac{1}{2}}$ is determined.

Near the equivalence point the ratio, ($[\text{Fe}^{3+}] / [\text{Fe}^{2+}]$) increases abruptly on addition of even a very small amount of the oxidant (titrant) leading to a sharp jump in the value of E_{cell} . After the equivalence point is passed, the ($\text{Fe}^{3+} / \text{Fe}^{2+}$) couple at the right hand electrode is replaced by the ($\text{Cr}_2\text{O}_7^{2-}, \text{H}^+ / 2 \text{Cr}^{3+}$) or ($\text{MnO}_4^-, \text{H}^+ / \text{Mn}^{2+}$) couple. Further addition of oxidant to the system, produces only small increase of E_{cell} .

A potentiometric titration curve may be obtained by plotting E_{cell} vs. volume (V) or number of drops (x) of standard solution of the oxidant added to a known volume of Fe^{2+} solution in acid medium. From the smooth curve, the volume, or, the number of drops of the titrant required to completely oxidise Fe^{2+} to Fe^{3+} may be determined by extrapolation. Hence the amount of oxidant required to oxidise half of the Fe^{2+} ions originally present may be calculated and the corresponding value of E_{cell} ($=E_{\frac{1}{2}}$) may be evaluated graphically.

Alternatively, the amount of oxidant corresponding to the equivalence point may be obtained from the maxima of the derivative plot of, $(\Delta E_{\text{cell}} / \Delta x)$, absolute against x (number of drops of oxidant). Volume (V) of the oxidant corresponding to the equivalence point may be obtained by finding the volume of a single drop of the titrant and multiplying by the number of drops required. Strength of the Fe^{2+} solution may now be calculated using the relation,

$$V_{\text{Fe}^{2+}} \times S_{\text{Fe}^{2+}} = V_{\text{oxidant}} \times S_{\text{oxidant}} \quad \dots \quad (5)$$

Thus, the E° value of $\text{Fe}^{3+}/\text{Fe}^{2+}$ system and also the concentration of a supplied solution of Fe^{2+} may be determined by potentiometric titration if a standard solution of an oxidant ($\text{K}_2\text{Cr}_2\text{O}_7 / \text{KMnO}_4$) and a standard reference electrode of known E° value are available.

Procedure :

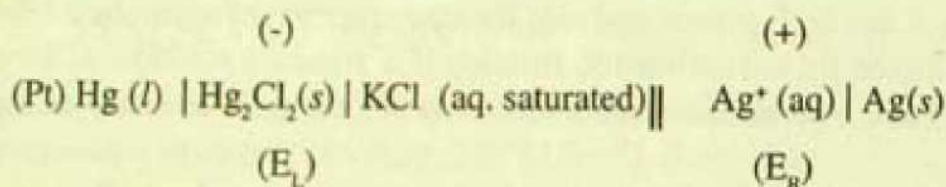
- Prepare 50 ml a standard (N/2) solution of $\text{K}_2\text{Cr}_2\text{O}_7$ by accurate weighing.
 - Prepare 50 ml of ($\sim \text{N}/10$) solution of Mohr's salt $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ in $\sim 2(\text{N}) \text{H}_2\text{SO}_4$.
- Take an aliquot of 10 ml of Mohr's salt solution in a beaker and dip a clean Pt electrode into this solution. Add sufficient volume of $\sim 2(\text{N}) \text{H}_2\text{SO}_4$ so that the electrodes dip in properly. Connect this half-cell with a saturated calomel electrode (SCE) through an agar-KCl (saturated) salt bridge. Complete the connections of this experimental cell with the potentiometer.
- Standardize the potentiometer with a standard cell.
- Measure the e.m.f. (E_{cell}) of the experimental cell.
- Add 2-3 drops of the standard (N/2) dichromate (or permanganate) solution, stir gently with a glass rod and record the E_{cell} . Repeat this procedure till the equivalence point is reached, which is indicated by a sharp increase of E_{cell} . Take a few more readings beyond the equivalence point.
- Plot (a) E_{cell} versus number of drops (x) of $\text{K}_2\text{Cr}_2\text{O}_7$ (or KMnO_4) solution,
 - $|\Delta E_{\text{cell}} / \Delta x|$ versus x (number of drops) and find the equivalence point, hence the value of E_{cell} corresponding to the half-neutralization point (i.e., E_{eq}) accordingly and calculate E° of the ($\text{Fe}^{3+}/\text{Fe}^{2+}$) system with the aid of the relation (4) using the literature value of E_{SCE} .
- Determine the number of drops of standard (N/2) $\text{K}_2\text{Cr}_2\text{O}_7$ (or KMnO_4) solution that constitute 1 ml of the solution, hence calculate the volume of the oxidant in ml required to reach the equivalence point. Finally calculate the strength of Fe^{2+} in the experimental solution using the relation (5).

Note : E_{SCE} at $t^\circ\text{C} = [0.2415 - 0.00076 (t - 25)]$ volt.

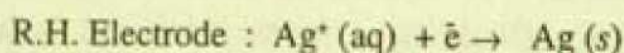
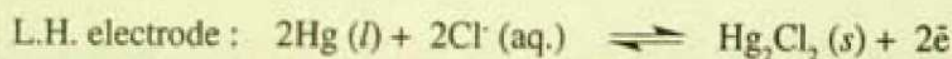
Experiment No. 7 : To titrate potentiometrically a standard solution of KCl against AgNO_3 solution and hence to determine (i) the concentration of AgNO_3 solution, and (ii) the solubility product of AgCl .

Theory :

When the $\text{Ag}^+/\text{Ag}(s)$ redox electrode is coupled with a saturated calomel electrode (SCE), KCl (satd.), $\text{Hg}_2\text{Cl}_2(s) \cdot \text{Hg}(l)$, the following electrochemical cell is produced :



where, the symbol, \parallel , stands for agar 2(M) NH_4NO_3 salt-bridge, which eliminates the liquid junction potential. The half cell reactions at the electrodes are :



The overall cell reaction is :



and the e.m.f. of the cell is given by :

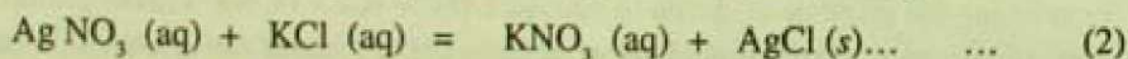
$$\begin{aligned} E_{\text{Cell}} &= E_R - E_L = E_{\text{Ag}^+/\text{Ag}} - E_{\text{SCE}} \\ &= E_{\text{Ag}^+/\text{Ag}}^\circ + 0.059 \log [a_{\text{Ag}^+} / a_{\text{Ag}(s)}] - E_{\text{SCE}} \quad (\text{at } 25^\circ\text{C}) \quad \dots \quad (1a) \end{aligned}$$

$\text{Ag}(s)$ being in the standard state, its activity will be unity. For a dilute solution activity (a) of Ag^+ ion may be replaced by the numerical value of its concentration $[\text{Ag}^+]$. Thus,

$$E_{\text{Cell}} = E_{\text{Ag}^+/\text{Ag}}^\circ + 0.059 \log [\text{Ag}^+] - E_{\text{SCE}} \quad \dots \quad (1b)$$

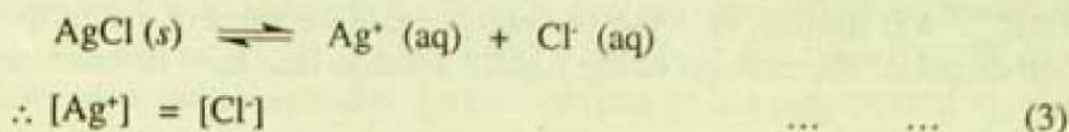
Since $E_{\text{Ag}^+/\text{Ag}}^\circ$ and E_{SCE} are fixed, E_{cell} depends on $[\text{Ag}^+]$.

As KCl solution is added to AgNO_3 solution, AgCl starts precipitating,



AgCl being sparingly soluble, $[\text{Ag}^+]$ decreases as more and more KCl solution is added, resulting in a decrease of E_{Cell} with increase in the number of drops (x) of KCl solution. Near the equivalence point, addition of a small volume (~1 drop) of KCl solution removes practically all the Ag^+ ions from the solution. This produces an abrupt decrease in E_{Cell} and

the $\Delta E_{\text{cell}} / \Delta x$ (absolute) value is also very large. Ag^+ ions present in the solution at the equivalence point come from the dissociation of the sparingly soluble AgCl produced :



The solubility product, K_{SP} , of AgCl may be defined according to :

$$K_{\text{SP}} = a_{\text{Ag}^+} \times a_{\text{Cl}^-} = [\text{Ag}^+][\text{Cl}^-] = [\text{Ag}^+]^2 \quad \dots \quad \dots \quad (4)$$

since for a dilute solution the activities may be replaced by the numerical values of concentrations.

$$\therefore [\text{Ag}^+] = (K_{\text{SP}})^{1/2} \quad \dots \quad \dots \quad (5)$$

Substituting this value of $[\text{Ag}^+]$ in eqn. (1b), one obtains the e.m.f. of the cell at the equivalence point :

$$E_{\text{cell}} (\text{eqv.}) = E_{\text{Ag}^+/\text{Ag}}^0 + 0.0295 \log K_{\text{SP}} - E_{\text{SCE}} \quad \dots \quad \dots \quad (6)$$

Thus, by determining E_{cell} at the equivalence point potentiometrically and knowing $E_{\text{Ag}^+/\text{Ag}}^0$ and E_{SCE} from literature, one may calculate K_{SP} using the relation :

$$K_{\text{SP}} = \text{anti log} \{ (E_{\text{cell}} (\text{eqv.}) + E_{\text{SCE}} - E_{\text{Ag}^+/\text{Ag}}^0) / 0.0295 \} \quad \dots \quad \dots \quad (7)$$

After the equivalence point is passed, further addition of KCl solution will lower the concentration of Ag^+ further, as a consequence of the constancy of K_{SP} ,

$$\therefore [\text{Ag}^+] = K_{\text{SP}} / [\text{Cl}^-] \quad \dots \quad \dots \quad (8)$$

Hence, E_{cell} will decrease with increase of $[\text{Cl}^-]$ according to,

$$\begin{aligned} E_{\text{cell}} &= E_{\text{Ag}^+/\text{Ag}}^0 + 0.059 \log K_{\text{SP}} - 0.059 \log [\text{Cl}^-] - E_{\text{SCE}} \\ &= E_{\text{Ag}^+/\text{Ag}}^f - E_{\text{SCE}} - 0.059 \log [\text{Cl}^-] \quad \dots \quad \dots \quad (9) \end{aligned}$$

where, $E_{\text{Ag}^+/\text{Ag}}^f$ represents the formal potential of



redox system and is given by :

$$E_{\text{Ag}^+/\text{Ag}}^f = E_{\text{Ag}^+/\text{Ag}}^0 + 0.059 \log_{10} K_{\text{SP}} \quad \dots \quad \dots \quad (10)$$

From the plot of E_{cell} vs. volume or number of drops (x) of KCl solution it is possible to find the volume (V) or the number of drops (x) of KCl required to completely precipitate the Ag^+ ions present in the solution and the value of E_{cell} at the equivalence point. The derivative plot, $(\Delta E_{\text{cell}} / \Delta x)$ absolute vs. x shows a maximum at the value of x corresponding to the equivalence point. The strength of the AgNO_3 solution may now be calculated using the relation :

$$V(\text{AgNO}_3) \times S(\text{AgNO}_3) = V(\text{KCl}) \times S(\text{KCl})$$

Thus, from potentiometric titration the strength of AgNO_3 solution and also the value of solubility product of AgCl may be determined.

Procedure :

1. Prepare an agar – 2(M) NH_4NO_3 salt bridge.
2. Prepare 100 ml of a standard (M/100) AgNO_3 solution in distilled water by accurate weighing.
3. Prepare 100 ml of a standard (M/10) KCl solution in distilled water by accurate weighing.
4. Take 10 ml of the prepared AgNO_3 solution in a 100 ml beaker and dip the silver electrode in this solution. Add sufficient amount of distilled water so that the electrodes dip in properly. This constitutes the experimental electrode ($\text{Ag}^+/\text{Ag}(s)$).
5. Set up the experimental cell by connecting the saturated calomel electrode (SCE) and the experimental electrode through the agar- NH_4NO_3 salt bridge.
6. Take the prepared KCl solution in a burette and determine the number of drops that constitutes 1 ml of solution.
7. Connect the experimental cell with the standardized potentiometer.
8. Measure the e.m.f. of the cell E_{cell} . Add 1-2 drops of KCl solution from the burette and record the e.m.f. Continue the procedure till a sharp change in E_{cell} takes place indicating the end point of the titration. Complete the titration by adding a few more drops of KCl solution beyond the end point. Record the volume (or, number of drops) of KCl and the E_{cell} values in a tabular form.
9. Plot (i) the observed E_{cell} values against number of drops (x) of KCl solution added, (ii) $(\Delta E_{\text{cell}} / \Delta x)$ (absolute value) versus x . Determine the equivalence point and the E_{cell} value at the equivalence point from the graph. Calculate the solubility product of AgCl using the literature value of $E^\circ_{\text{Ag}^+/\text{Ag}}$ and E_{SCE} .
10. Calculate the strength of the AgNO_3 solution by using the volume of standard KCl solution required at equivalence point (obtained graphically) and compare this with the strength obtained from direct weighing.

Note : E_{SCE} at $t^\circ\text{C} = [0.2415 - 0.00076 (t - 25)]$ volt. $E^\circ (\text{Ag}^+ / \text{Ag}(s)) = + 0.799$ volt at 25°C .

(d) Experiments based on colourimetry

Introduction :

When light is incident upon a body it may undergo reflection, absorption and transmission. The wavelength(s) of light which a particular substance absorbs depend(s) upon its chemical constitution and to a certain extent on the environment in which the substance is placed. Each substance has its own characteristic absorption spectrum which depends critically on the quantised energy levels available and their quantum mechanical description.

Experiment No. – 8 : To test the validity of Lambert – Beer's Law for $K_2Cr_2O_7$ / $KMnO_4$ and hence to determine the concentration of the given solution of the substance colourimetrically.

Theory : Lambert – Beer's Law states that when a monochromatic beam of light passes through a homogeneous solution of a substance which absorbs the radiation, the rate of decrease of intensity of radiation with thickness (l) of the absorbing solution is proportional to the intensity (I) of the incident radiation as well as on the concentration (c) of the light absorbing species in solution, which may be expressed according to,

$$- dI / dl = kcl \quad \dots \quad \dots \quad \dots \quad (1)$$

where k is a proportionately constant. The relation (1) means that the intensity of radiation (I) is reduced by an amount dI on passing through a length, dl , of the solution of concentration c (assumed to be uniform throughout the solution). Separating the variables, one obtains,

$$- dI / I = k c (d l) \quad \dots \quad \dots \quad \dots \quad (2)$$

Integrating the differential equation (2) with proper limits when, $l = 0$, $I = I_0$ the intensity of the incident light, and when, $l = l$, $I = I_t$, the intensity of the transmitted light, one obtains,

$$\ln (I_t / I_0) = - k c l \quad \dots \quad \dots \quad \dots \quad (3)$$

Transforming the logarithmic term to base 10 (i.e., \log_{10}) one obtains,

$$\log_{10} (I_t / I_0) = - (k / 2.303) c l \quad \dots \quad \dots \quad (4)$$

$$\therefore I_t = I_0 \times 10^{-\epsilon c l} \quad \dots \quad \dots \quad (5)$$

$$\text{where, } \epsilon = k/2.303$$

The term, Optical Density (OD) or Absorbance (A) is defined as

$$OD = A = \log_{10} (I_0 / I_t).$$

$$\text{Thus, } OD = A = \epsilon c l \quad \dots \quad \dots \quad \dots \quad (6)$$

where, ϵ is the *molar extinction coefficient* of the light absorbing species and l is the optical path length in cm. of the solution of concentration c moles.lit⁻¹, through which the absorbing radiation passes, so the unit of ϵ is mol⁻¹.lit.cm⁻¹. Eqn (6) is the mathematical expression for *Lambert-Beer's Law*.

The quantity ϵ is characteristic of the absorbing species (molecule or ion) and depends on temperature and the wavelength of radiation. Thus, when a solution of an absorbing species is scanned through a range of wavelengths (λ), it is observed that a plot of ϵ versus λ (in nm) shows characteristic maxima at specific wave lengths. The wavelengths at which ϵ passes through maxima are called absorption maxima, λ_{max} of the species.

When the solution of a substance obeys the Lambert-Beer's Law, in a particular concentration range, the optical densities (or absorbances) of a series of such solutions of different concentrations at a fixed path length (l) will show a linear dependence on the molar concentration (c). That is, a plot of A versus c will be a straight line passing through the origin with a positive slope equal to ϵl (Fig. 1). When $l = 1$ cm, the slope directly gives ϵ .

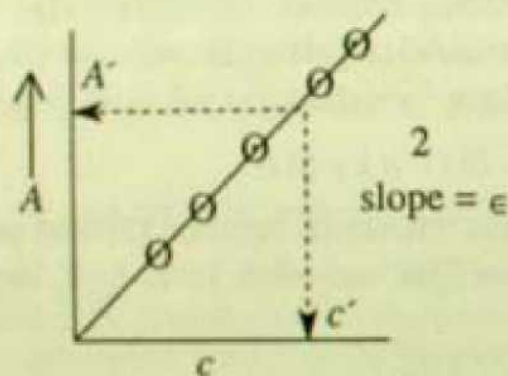


Fig. 1 : Verification of Lambert-Beer Law

This A versus c curve (Fig. 1) called a calibration curve, may be used to measure an unknown concentration (c') of the solution of the same substance by measuring its absorbance (A') at the same wavelength using the same path length.

Procedure :

1. Prepare 500 ml ~ 1(N) H_2SO_4 solution in a stoppered bottle.

2. Prepare 100 ml of standard (M/50) solution of $K_2Cr_2O_7$ in the $\sim 1(N)$ H_2SO_4 in a volumetric flask by accurate weighing. From this standard solution, prepare 100 ml of $10^{-3}(M)$ $K_2Cr_2O_7$ solution in $\sim 1(N)$ H_2SO_4 by exact dilution.

2(a) For $KMnO_4$ solution, prepare 100 ml of approximately $\sim(M/50)$ $KMnO_4$ solution in distilled water and standardize the same by usual titrimetric method against a standard (N/10) oxalic acid solution in 2(N) H_2SO_4 medium at 60-70°C (see Ch-4). From this standardized (M/50) $KMnO_4$ solution, prepare 100 ml of $10^{-3}(M)$ $KMnO_4$ solution in water by exact dilution.

3. Prepare the following sets of solutions, as required, in standard-sized test tubes.

Vol. of $K_2Cr_2O_7$ or $KMnO_4$ (ml) :	1	2	3	4	5	6	7	8	9
Vol. of 1(N) H_2SO_4 or water (ml) :	9	8	7	6	5	4	3	2	1
4. For the dichromate solution, set the wavelength at around 475 nm and for the permanganate solution set the wavelength at around 530 nm in the colorimeter / spectrophotometer.
5. Set zero of the colorimeter by adjusting the dark current. Insert the cell filled with water and adjust the transmittance (T) to 100%.
6. Fill the other cell successively with the prepared sets of solutions and measure their transmittances, each time rinsing the cell with the experimental solution.
7. Calculate the absorbances (A) of the solutions using the relation :

$$A = \log \frac{100}{T(\%)} = 2 - \log T(\%)$$

8. Plot A versus concentration and draw the best straight line passing through the origin and the experimental points to verify Lambert-Beer's Law, and estimate ϵ (molar extinction coefficient) from the slope knowing the optical path length (usually 1 cm.).
9. Measure the absorbance (A) of the unknown solution of the substance ($K_2Cr_2O_7$ or $KMnO_4$ as the case may be). From the calibration curve of A versus concentration (Fig. 1) find the concentration (c) of the unknown solution.

Note : Lambert-Beer's Law has a number of limitations. It is usually found that at high concentrations the substances absorb much more than what the equation (6) describes, as such the calibration curve becomes non-linear at high concentrations. Thus, Lambert – Beer's Law may be applied only for sufficiently dilute solutions.

Experiment No. 9 : To determine the pK_{in} value of an acid-base indicator by colourimetric method

Theory :

Acid base indicators are weak acids or bases having distinctly different colours in acidic and alkaline solution, and by virtue of change of colour they indicate the end points of acid-base titrations. The ionisation equilibria of a weak acid indicator (HIn) may be represented according to,



for which the ionisation constant (K_{in}) in dilute solution may be defined as the concentration quotient (2).

$$K_{in} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]} \quad \dots \dots (2)$$

where, []'s represent the molar concentrations of the respective species. Transforming the eqn. (2) in logarithmic form one obtains,

$$\text{pH} = \text{p}K_{in} + \log \frac{[\text{In}^-]}{[\text{HIn}]} \quad \dots \dots (3)$$

(where, $\text{p}K_{in} = -\log_{10} K_{in}$ and $\text{pH} = -\log_{10} [\text{H}^+]$ in dilute solution).

Thus, if a fixed amount of the indicator is placed in the same volume of a series of buffer solutions of different known pH values, the ratio, $[\text{In}^-] / [\text{HIn}]$, will increase with increase of pH. If the values of the ratio at different pH are determined by measuring the colour intensity of the indicator solutions, then the $\text{p}K_{in}$ value of the indicator can be found out if the pH of the buffer solutions are known.

If the alkaline form of the indicator (In^-) absorbs at a selected wave length and Beer's Law is obeyed in the range of concentration of the indicator used, then the absorbance (A) of the indicator solution at a particular pH will be proportional to its concentration, provided the acid form (HIn) does not absorb at this wave length.

$$A = \epsilon \cdot [\text{In}^-] \cdot l \quad \dots \dots (4)$$

In a strongly alkaline solution, HIn is practically absent, and the absorbance (A') will correspond to the total concentration (T_{in}) of the indicator.

$$A' = \epsilon \cdot T_{in} \cdot l \quad \dots \dots (5)$$

where, ϵ = molar extinction coefficient of In^- and l = optical path length in cm.

Mass balance equation of the indicator is,

$$T_{\text{In}} = [\text{HIn}] + [\text{In}^-] \quad \dots \dots (6)$$

$$\therefore [\text{HIn}] = T_{\text{In}} - [\text{In}^-] \quad \dots \dots (6a)$$

from (5) – (4) one obtains,
$$\frac{(A' - A)}{\epsilon \cdot l} = [\text{HIn}] \quad \dots \dots (7)$$

From (4) one obtain,
$$\frac{A}{\epsilon \cdot l} = [\text{In}^-] \quad \dots \dots (7a)$$

Substituting these values of $[\text{HIn}]$ and $[\text{In}^-]$ in eqn (3) one obtains,

$$\text{pH} = \text{pK}_{\text{In}} + \log_{10} \left(\frac{A}{A' - A} \right) \quad \dots \dots (8)$$

A and A' may be measured colourimetrically. Therefore, by plotting $\log_{10} [A/(A' - A)]$ against pH of the buffer solutions a straight line of slope = 1 will be obtained, of which the intercept on the pH axis will give pK_{In} .

Procedures : (for Bromocresol green indicator).

1. Prepare 100 ml of exact 0.4(N) acetic acid ($\text{pK}^{\text{H}} = 4.74$ at 25°C) and 100 ml of exact 0.4(N) NaOH solutions separately by usual procedure. (cf Expt. Nos. 3 & 4).
2. Take 12 hard glass test tubes of uniform dimensions and label them from 1 to 12. Prepare the following series solutions by proper mixing (experimental pH values may be obtained from chart below, or, may be determined using a pH meter).

Test tube	Vol. of 0.4(N) acetic acid (ml)	Vol. of 0.4(N) NaOH (ml)	Vol. of water (ml)	pH (experimental)
1	5.0	0.5	4.5	3.72
2	5.0	1.0	4.0	4.05
3	5.0	1.5	3.5	4.27
4	5.0	2.0	3.0	4.45
5	5.0	2.5	2.5	4.63
6	5.0	3.0	2.0	4.80
7	5.0	3.5	1.5	4.99
8	5.0	4.0	1.0	5.23
9	5.0	4.5	0.5	5.57

In test tube numbers 10 to 12, take 2.5 ml of 0.4(N) NaOH and add 7.5 ml of water.

3. Add a few (~ 3-4) drops of bromocresol green indicator to test tube number 10 using a dropper.
4. Set the colorimeter at 570 nm, adjust the transmittance of water to 100%.
5. Measure the transmittance of the solution in test tube 10. If the transmittance is below 15%, take test tube 11 and add fewer number of drops of the indicator to it and measure the transmittance. In this way by adjusting the numbers of drops of the indicator, adjust the transmittance of the alkaline form between 25 to 15% using test tube nos. 10-12 as required.
6. Add the same number of drops of the indicator as adjusted in step 5 to each of test tubes 1-9 and measure their transmittances.
7. Calculate the absorbance (A) values of solutions 1-9 and the absorbance (A') of the alkaline solution of the indicator (10, 11 or 12) using the relation :

$$A = \log (100/T\%) = 2 - \log T.$$
8. Plot $\log_{10}[A / (A' - A)]$ against pH and draw the best straight line of unit slope passing through the experimental points, using the same scale for pH and $\log_{10}[A / (A' - A)]$ axis. Find pK_{in} from the intercept on the pH axis.

Experiment No. 10 : To study the kinetics of the reaction between $S_2O_8^{2-}$ and I^- by colourimetric method.

Theory :

They overall reaction between $S_2O_8^{2-}$ and I^- is



If a equivalent / litre of both the reactants, $S_2O_8^{2-}$ and I^- are mixed, and if n be the overall order of the reaction, then the time t required for a definite fraction of the reactants to react will be inversely proportional to a^{n-1} i.e.,

$$t \propto 1 / a^{n-1} \dots \dots \dots (2)$$

Thus, if a_1 and a_2 equivalent/litre be the two starting concentrations of the two reactants and t_1 and t_2 be the times required for a definite fraction of the reactants to react, then, according to eqn (2),

$$(t_1 / t_2) = (a_2 / a_1)^{n-1} \dots \dots \dots (3)$$

On taking logarithm and rearranging, the eqn. (3) is transformed to (4) which gives the order of the reaction, n ,

$$n = 1 + \frac{\log(t_1 / t_2)}{\log(a_2 / a_1)} \quad \dots \dots \dots (4)$$

Experimentally the value of n is found to be 2, i.e., the reaction (1) is a second order reaction, being first order in $[S_2O_8^{2-}]$ and first order in $[I^-]$ and the rate law may be expressed according to,

$$\text{rate} = -\frac{d[S_2O_8^{2-}]}{dt} = k[S_2O_8^{2-}][I^-] \quad \dots \dots \dots (5)$$

where, k = second order rate constant in $\text{eqv}^{-1} \cdot \text{lit. s}^{-1}$.

If x equivalent / litre of $S_2O_8^{2-}$ has reacted by the time t , then, the rate law eqn. (5) takes the form :

$$\frac{dx}{dt} = k(a - x)^2 \quad \dots \dots \dots (6)$$

Since at $t = 0$, $x = 0$ and at $t = t$, $x = x$, the eqn. (6) on integration takes the form (7)

$$\frac{x}{a(a - x)} = kt \quad \dots \dots \dots (7)$$

Since one of the product, I_2 , is coloured ($\lambda_{\text{max}} = 525 \text{ nm}$) its absorbance A_t at any instant of time (t) is proportional to its concentration (x), provided Beer's Law is obeyed. The eqn. (7) is then transformed to :

$$kt = \frac{1}{a} \cdot \frac{A_t}{A_\infty - A_t} \quad \dots \dots \dots (8)$$

where, A_t and A_∞ are the absorbance values at $t = t$ and $t = \infty$ respectively. On rearrangement, one obtains,

$$\frac{1}{A_t} = \frac{1}{A_\infty} + \frac{1}{akA_\infty} \cdot \frac{1}{t} \quad \dots \dots \dots (9)$$

Thus, a plot of $(1/A_t)$ against $(1/t)$ will give a straight line with intercept equal to $(1/A_\infty)$ and slope equal to $(1/akA_\infty)$ from which the value of the rate constant, k , may be evaluated using the relation :

$$k = (\text{intercept}) / (a \times \text{slope}).$$

Procedure :

1. Prepare 100 ml of a standard (N/10) $K_2Cr_2O_7$ and 100 ml of a standard KI (strength $> N/10$) solutions by accurate weighing. Prepare 100 ml of a $K_2S_2O_8$ solution ($> N/10$) and 250 ml of a ($\sim N/10$) sodium thiosulfate solution by weighing with a rough balance.
2. Standardize the thiosulfate solution against the standard (N/10) dichromate following the usual procedure. (cf. ch.. 5)
3. Take 10 ml of the prepared $K_2S_2O_8$ solution in a 500 ml conical flask, add 10 ml of 10% (w/v) KI solution and 2 ml of glacial acetic acid. Cover the conical flask with watch glass and keep the mixture in dark for 25 ~ 30 minutes. Add 80 ml distilled water and then titrate the liberated iodine with the standard ($\sim N/10$) thiosulfate solution using starch indicator. Calculate the strength of the $K_2S_2O_8$ solution. Prepare an exact (N/10) $K_2S_2O_8$ solution by accurate dilution this solution.
4. Similarly prepare an exact (N/10) KI solution by exact dilution of the prepared standard ($> N/10$) KI solution.
5. Mix the $K_2S_2O_8$ and KI solutions as follows, one at a time, and note the time of half discharge of any one of the reactants in each case.

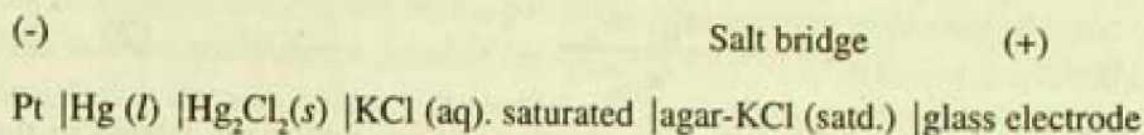
	(N/10) KI solution (ml)	(N/10) $K_2S_2O_8$ (ml)	H ₂ O (ml)
Set I	10	10	0
Set II	5	5	10

6. Record the absorbance (A_t) of these two sets of solutions at 525 nm wavelength at an interval of about 2-3 minutes for both the sets.
7. Plot A_t against t for each of two sets. Select any A_t for Set I and find the corresponding time t_1 from the graph. Similarly from the graph of Set II find the time t_2 for the value of A_t that is just half of the A_t chosen for Set I. Calculate the order (n) of the reaction using the relation (4).
8. Plot $1/A_t$ against $1/t$ for both the sets and find k from the slopes and intercepts of the resulting straight lines.

(e) Experiments based on pH-metry

Measurement of pH using Glass-Calomel electrode pH Meter :

The pH of an aqueous solution can be measured using glass-calomel electrode system in which following electrochemical cell is formed :



The left-hand electrode is the saturated calomel electrode (SCE) and the right hand electrode is the glass electrode which is actually an *ion selective membrane electrode* whose potential is reversible with respect to H^+ ions. The construction of the glass electrode is based on the observation that the electric potential difference between a glass surface and an aqueous solution varies regularly with pH of the aqueous solution except those which are very strongly acidic or very strongly alkaline. The electrode is made of a thin walled bulb of low melting glass of high electrical conductivity. Inside the bulb is placed a solution of constant pH (a buffer solution, or, 1(N) HCl solution) together with a little quinhydrone and a platinum wire for electrical contact. The potential (E_g) of the glass electrode at 25°C may be expressed according to,

$$E_g = E_g^\circ + 0.059 \log a_{\text{H}^+} = E_g^\circ - 0.059 \text{ pH} \quad \dots \quad (1)$$

For actual pH measurement, the glass electrode is standardised in buffer solutions of known pH values. Usually potassium hydrogen phthalate (pH, 4), phosphate (pH, 7) and borax (pH, 9.2) buffer solutions are used for calibration of pH meter.

The e.m.f. (E_{cell}) the glass-calomel electrode cell is given by,

$$E_{\text{cell}} = E_g - E_{\text{SCE}} = E_g^\circ - 0.059 \text{ pH} - E_{\text{SCE}} \quad \dots \quad (2)$$

$$\therefore \text{pH} = (E_g^\circ - E_{\text{SCE}} - E_{\text{cell}}) / 0.059 \quad \dots \quad (3)$$

The pH value can be read off directly from the digital pH-meter calibrated with standard buffer solutions.

Experiment No. 11 : Determination of pK^H value of a weak acid by pH-metric method.

Ionisation of a weak acid (HA) in aqueous solution may be represented according to,



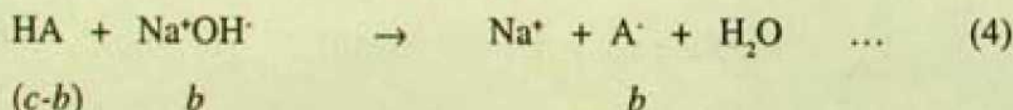
of which the ionisation constant (K^H) is given by the activity quotient of the ionisation equilibrium (1),

$$K^H = \frac{a_{H^+} \cdot a_{A^-}}{a_{HA}} \quad \dots \quad (2)$$

where, a 's represent activities of the respective species which are related to the molar concentration, (c), according to $a = c \cdot f$, where, f = activity coefficients. In dilute aqueous solutions of weak acids, ionic strength is very low, so the activity coefficients approach unity, hence, the concentrations approach activities. Consequently the ionisation constant (K^H) may be expressed as concentration quotients of ionisation equilibrium (1), according to,

$$K^H = \frac{C_{H^+} \cdot C_{A^-}}{C_{HA}} \quad \dots \quad (3)$$

When an amount ($b \text{ mol.lit}^{-1}$) of a strong base (e.g., NaOH) is added to the solution containing a known amount ($c \text{ mol.lit}^{-1}$) of the weak acid (HA), so that, $b < c$, the acid is partly neutralized to form b amount of the salt, Na^+A^- , which remains completely ionised in the solution, that still contains $(c - b)$ amount of the acid HA.



Such a mixture of a weak acid (HA) with its salt (Na^+A^-) constitutes a *buffer solution*, which has the ability to resist the change of H^+ ion concentration when small amount of an acid or a base is added to it. Expressions for pH of such a buffer solution are the different forms of the *Henderson Equation* (5 a,b,c), which may be obtained by substituting the values of C_{A^-} ($= b$) and C_{HA} ($= c - b$) in the expression (3) for K^H , and transforming to logarithmic forms :

$$pH = pK^H + \log_{10} \frac{C_{A^-}}{C_{HA}} \quad \dots \quad (5a)$$

$$pK^H + \log_{10} \frac{b}{c - b} \quad \dots \quad (5b)$$

$$pK^H + \log_{10} \frac{[\text{Salt}]}{[\text{Acid}]} \quad \dots \quad (5c)$$

If the amount of base added is just half-equivalent of the acid present, i.e., when $b = c/2$, then the eqns. (5 a,b,c) are transformed to,

$$pK^H = (pH)_{1/2} \quad \dots \quad (6)$$

where, $(pH)_{1/2}$ means the pH of the solution at the half neutralization point. pK^H value of a weak acid is most conveniently determined by pH metrically titrating a known amount of the acid in aqueous solution with a strong base of known strength. A pH metric titration curve may be constructed by plotting the pH of the acid solution after each addition of the strong base and the equivalence point of the titration may be determined graphically. The pH of the solution corresponding to the half the neutralization point may be read out from the pH titration curve. This is how the pK^H value can be determined.

Procedure :

1. (a) Prepare 250 ml of a standard (N/20) solution of oxalic acid by accurate weighing.
 (b) Prepare 50 ml of ($\sim N/2$) NaOH solution. Pipette out 10 ml of this solution into a 100 ml volumetric flask, dilute to the mark and mix uniformly to get a ($\sim N/20$) NaOH solution.
 (c) Prepare 100 ml of ($\sim N/20$) acetic acid solution.
2. (a) Titrate 25 ml of the standard (N/20) oxalic acid solution with the ($\sim N/20$) NaOH solution using phenolphthalein indicator and find the actual strength of the ($\sim N/20$) NaOH and finally that of ($\sim N/2$) NaOH solution.
 (b) Titrate 25 ml of the ($\sim N/20$) acetic acid with the standard ($\sim N/20$) NaOH solution using phenolphthalein indicator and find the actual strength of the acetic acid solution.
3. To set up the pH-meter, the glass electrode and the saturated calomel electrode are to be dipped in distilled water for \sim half an hour before the start of the experiment.
4. Prepare standard buffer solution of pH = 4 and pH = 7 by dissolving the corresponding pH tablets in the specified volume of distilled water.
5. Standardize the pH meter by alternately dipping the glass – calomel electrode assembly in pH = 4 and pH = 7 buffer solutions and adjusting the instrument accordingly at the experimental temperature.
6. Take 25 ml of (N/20) acetic acid solution in a 100 ml beaker. Add sufficient quantity of distilled water so that the electrodes dip into it properly. Dip the electrodes of the pH meter gently in to this solution, allow the system to attain the equilibrium at the experimental temperature and record the pH.

7. Add 1-2 drops of the (N/2) NaOH solution from a burette (micro burette) stir gently to mix uniformly and record the pH. Repeat the process until the end-point is reached (indicated by sharp rise in the pH). Record the pH and the number of drops of the titrant in a tabular form. Take a few more readings beyond the end point.
8. Determine the number of drops per ml of the titrant solution and calculate the titre value.
9. Plot (i) pH vs. number of drops (n) of the (~N/2) NaOH solution added and (ii) $\Delta \text{pH} / \Delta n$ versus n. From the graphs, determine the equivalence point and hence the strength of the acetic acid solution.
10. From the pH vs. n plot determine the pH at the half neutralization point which will be equal to the pK^{H} of the acid.

Note :

(1) For ionisation of a weak monoprotic acid (HA), the equilibrium concentrations of H^+ ion and A^- ion are equal, i.e., $C_{\text{H}^+} = C_{\text{A}^-}$, and the equilibrium concentration of unionised acid is practically equal to the analytical concentration (c) of the acid. For such a weak acid, the expression (3) for K^{H} is simplified to

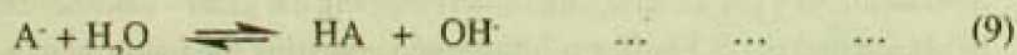
$$K^{\text{H}} = \frac{C_{\text{H}^+} \cdot C_{\text{A}^-}}{C_{\text{HA}}} = \frac{(C_{\text{H}^+})^2}{c} \quad \dots \dots (7)$$

which may be transformed to,

$$\text{pH} = \frac{1}{2} \text{pK}^{\text{H}} - \frac{1}{2} \log c \quad \dots \dots (8)$$

which gives the pH of the solution of the weak acid, where, $\text{pH} = -\log_{10} C_{\text{H}^+}$ ($= -\log_{10} a_{\text{H}^+}$ precisely) and $\text{pK}^{\text{H}} = -\log_{10} K^{\text{H}}$.

(2). When an equivalent amount of base is added to the acid solution, i.e., when $b = c$, the concentration of the salt formed is equal to c. The conjugate base A^- of the weak acid (HA) being strong, undergoes hydrolysis according to,



$$(\therefore C_{\text{HA}} = C_{\text{OH}^-})$$

pH of such a solution, ignoring the volume change, may be expressed by the eqn. (10)

$$\text{pH} = \frac{1}{2} \text{pK}_{\text{w}} + \frac{1}{2} \text{pK}^{\text{H}} + \frac{1}{2} \log c \quad \dots \dots (10)$$

where, K_w = ionic product of water ($K_w = C_{H^+} \cdot C_{OH^-}$) at the experimental temperature. At 25°C, $K_w = 10^{-14}$, hence the eqn. (10) is transformed to,

$$pH = 7 + \frac{1}{2} pK^H + \frac{1}{2} \log c \quad \dots \quad \dots \quad \dots \quad (10a)$$

(3). pK^H value of the weak acid can also be determined by measuring the pH values of a series of solutions of known concentrations of the acid without any added base using the eqn. (8) and also by measuring the pH of a series of solution known concentrations of the salt of the weak acid with a strong base using the relation (10a). But the method of half neutralization point, $pK^H = (pH)_{\frac{1}{2}}$, is the one most convenient and accurate.

(f) Experiments Based on Phase Rule

Experiment No. 12 : Study of the phase diagram of a binary system (phenol-water) and the effect of impurities (eg. NaCl).

Theory :

A diagram representing the conditions of equilibrium among different forms or phases of a substance or of a mixture of substances is called a phase diagram. When the position of such an equilibrium is influenced only by such variables as temperature, pressure and concentration, but not by such factors as gravity, surface tension, electrical and magnetic forces, the number of degrees of freedom (F) of the system may be related to the number of components (C) and the number of phase (P) according to the *Phase Rule* equation.

$$F = C - P + 2$$

In a binary mixture of two partially miscible liquids e.g., phenol and water, two phases are formed. When phenol is gradually added to water, phenol passes into solution until a saturated solution of phenol in water is obtained. A new phase of higher density, consisting of a saturated solution of water in phenol appears on addition of further quantities of phenol. Increase in the concentration of phenol increases the volume of the second phase (i.e., water in phenol) and decreases the volume of the first phase (i.e., phenol in water), but the relative concentrations of the components in either phase remain constant. Such mutually saturated liquid pairs in contact with the vapour phase constitutes an *invariant system*, the only variable being the temperature. Rise of temperature brings about a change in the mutual solubilities of the two liquids, which can be measured by placing known weights of the two liquids in

stoppered tubes and observing the temperature at which the boundary between the two liquid phases disappears. The solubility curve of phenol water system (Fig. 1) shows that the mutual solubilities increase with increase of temperature. The two phases has an unique

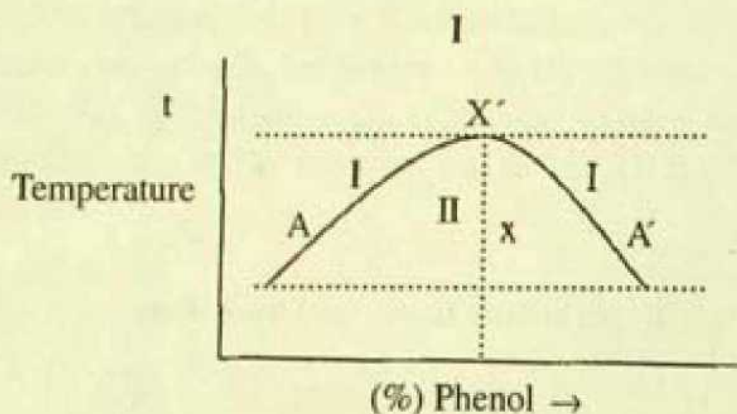


Fig. 1. Solubility curve of phenol-water system

composition called *consolute composition* at a certain temperature (t_c) called *critical solution temperature (CST)*, or, *consolute temperature (CT)*, at which they form a single phase. For phenol water system $t_c = 65.9^\circ\text{C}$ is specifically the *upper critical solution temperature (UCST)* and the consolute compositions is, phenol = 34% and water = 66%. Above this temperature the two liquids are completely miscible. Compositions of the liquid pair indicated by any point (x) in between the two solubility curves will separate into two phases (II) indicated by two points A and A', while any composition represented by the points out side the area under the curves will form a single phase (I). Lines (such as A A') joining the two mutual solubilities at any given temperature are called *tie-lines* and the two solutions represented by the compositions A and A' are called *conjugate solutions*.

Since the regions (I) out side the solubility curves consist of only one liquid phase, so $P = 1$, $C = 2$ (water and phenol), hence, $F = C - P + 2 = 2 - 1 + 2 = 3$. That is, such a system a will be *trivariant*. Since, pressure is fixed (i.e., 1 atmos.), only two degrees of freedom remain, i.e., temperature and concentration, which should be specified in order to define the system completely. In the regions (II) under the solubility curves, there are two phases, i.e., $P = 2$, $C = 2$ (as before), hence, $F = C - P + 2 = 2 - 2 + 2 = 2$. That is, such systems will be *bivariant*. So if the pressure is fixed (i.e., 1 atmos.), the temperature alone will define the system completely. Therefore, the two phases at any given temperature will have definite compositions, irrespective of their amounts.

At any point on the solubility curves, say at A or A', only a saturated solution of fixed composition is present i.e., $C = 1$ and $P = 1$, hence, $F = C - P + 2 = 1 - 1 + 2 = 2$, i.e., if the pressure is fixed (1 atmos.), solubility has a definite value at a particular temperature.

At the point x' on this curve, the two liquids have identical composition i.e., saturated solution of phenol in water = saturated solution of water in phenol at temperature t_c , i.e., $C = 1$, $P = 2$, hence, $F = C - P + 2 = 1 - 2 + 2 = 1$. The pressure being kept fixed (i.e., 1 atmos.), the system represented by this point x' is *invariant*, since temperature (t_c) and compositions are automatically fixed.

When a third substance, such as, NaCl is added to a binary mixture of two partially miscible liquids (e.g., phenol-water), the 2-component system ($C = 2$) changes to a 3 component system ($C = 3$), in which the mutual solubility of the liquids will depend upon the chemical nature and quantity of the third substance. Mutual solubilities generally decrease when the third substance is soluble only in one of the two liquids, and consequently consolute temperature rises. When the third substance dissolves in both the liquids consolute temperature is generally lowered.

Procedure :

1. Weigh out accurately 2-3 g of phenol (**Caution, Corrosive**) from a weighing bottle into a hard glass test tube.
2. Add 1 ml of water (or 0.5% NaCl solution as the case may be) to it from a burette. Clamp the test tube inside a large beaker fitted with a glass stirrer. Insert a thermometer into the test tube. Pour sufficient amount of water in the beaker.
3. Heat the water in the beaker uniformly, while stirring it all the time. The mixture in the test tube which was initially turbid, becomes suddenly clear at a particular temperature. Note the temperature. Allow the whole system to cool. Record the temperature at which turbidity again reappears. Take the mean of these two temperatures (disappearance and reappearance).
4. Go on adding 1 ml portions of water (or 0.5% NaCl solution as the case may be) and at each step note the temperature for disappearance and reappearance of turbidity, until about 16 ml of water (or 0.5% NaCl solution) has been added.

5. Find the weight percentages of phenol in the mixture from the known weights of phenol and water (density of water (or solution) ~ 1 g/ml).
6. Draw the solubility curve by plotting the mean of the temperature for the appearance and disappearance of turbidity against percentage of phenol. Determine the upper critical solution temperature and the consolute composition for the system and interpret your results.

Note :

- i) 0.1(M) KCl raises the CST of phenol-water system by $\sim 8^\circ\text{C}$.
- ii) Succinic acid lowers the CST of phenol-water system.
- iii) CST of phenol-water system is raised by $\sim 12.3^\circ\text{C}$ if D_2O is used in place of ordinary water, H_2O .

Chapter - 11

Titrimetric Estimations of Single Compound / Constituent / Parameter (Inorganic / Organic / Biochemical / Industrial Samples)

Experiment – 1 : Estimation of total hardness of water sample by complexometric EDTA Titration.

Principle :

Hardness of water is of two types - temporary hardness and permanent hardness. Temporary hardness is due to dissolved bicarbonates and permanent hardness is due dissolved chlorides and sulphates, mainly of Ca^{2+} , Mg^{2+} and Fe^{2+} . Hardness is expressed in terms of ppm of CaCO_3 (i.e. mg. of CaCO_3 per 1000 ml of sample water).

Total hardness may be estimated complexometrically by titrating a known volume of the water sample with a standard EDTA solution in NH_4Cl - NH_3 buffer medium (pH 10) using Eriochrome Black - T (EBT) indicator.

EDTA, ethylenediamine tetraacetic acid, is commercially obtained as its disodium salt, $\text{Na}_2\text{H}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$. It reacts with metal ions ($\text{M}^{2+} = \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Fe}^{2+}$) to form stable 1:1 complexes.



$$\therefore \text{EDTA} \equiv \text{M}^{2+} \equiv \text{CaCO}_3$$

$$\therefore 1000 \text{ ml of (M) EDTA} \equiv 100 \text{ g. of CaCO}_3 \equiv 100,000 \text{ mg. of CaCO}_3$$

$$\therefore 1 \text{ ml of (M) EDTA} \equiv 100 \text{ mg. of CaCO}_3$$

Chemicals required :

- Standard (M/100) solution of A. R. zinc-acetate dihydrate, $\text{Zn}(\text{OOCCH}_3)_2 \cdot 2\text{H}_2\text{O}$ (F.W. = 219.38). Place 5 g. of A.R. NH_4Cl in a 250 ml volumetric flask and dissolve the salt in ~50 ml of distilled (or deionised) water. Weigh out accurately ~0.5 – 0.6 g (w) of zinc acetate dihydrate and transfer the same quantitatively into the volumetric flask. Shake to dissolve the salt in the NH_4Cl buffer solution. Make up to the mark with distilled / deionised water and shake thoroughly to mix uniformly.

The strength of the solution will be = $(w / 0.54846) (M/100)$.

- b) $(M/100)$ solution of (A.R.) $\text{Na}_2\text{H}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ (Mol. Wt. 372.24) :

Prepare by dissolving about 0.9 -1.0 g (exactly 0.9306 g) of the salt in distilled / deionised water and dilute to 250 ml.

- c) $\text{NH}_4\text{Cl} - \text{NH}_3$ buffer solution of pH 10 containing a small amount of Mg (EDTA) complex.

(i) Dissolve 17.5 g of A.R. NH_4Cl in 142ml of concentrated NH_3 (sp. gr. 0.88 - 0.90).

(ii) Dissolve 1.179 g of $\text{Na}_2\text{H}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ and 0.78 g. of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in 50 ml distilled / deionised water.

Mix the solutions (i) and (ii) and dilute to 250ml with distilled deionised water. Use 5 ml of this buffer solution for titration of 50 ml of water samples.

- d) Eriochrome Black-T (EBT) indicator : Prepare 0.4% methanolic solution of the dyestuff. The solution is stable for ~ one month.

Alternatively, grind a mixture of 0.05 g of the dyestuff with 5.0g of (A.R.) KNO_3 or KCl or NaCl in a glass or porcelain mortar. The mixture contains ~1% of the indicator. Use 30 - 50 mg of the indicator mixture for titration of 50 ml of water samples.

Procedure :

1. *Standardisation of EDTA solution :*

Pipette out 25 ml of standard zinc acetate solution in a 250 ml conical flask, add 20 ml of distilled/ deionised water, 5 ml of $\text{NH}_4\text{Cl} - \text{NH}_3$ buffer solution and a pinch of EBT indicator powder (or 8-10 drops of the indicator solution). Colour of the solution turns wine red. Titrate the solution with the EDTA solution till the wine red colour turns blue. (Titre = V_1 ml)

2. *Estimation of total hardness of water sample:*

Take an aliquot of 50 ml of the water sample in a 250 ml conical flask, add 5 ml of $\text{NH}_4\text{Cl} - \text{NH}_3$ buffer solution and a pinch of EBT indicator powder (or 8-10 drops of the indicator solution). Colour of the solution turns wine red. Titrate the solution with the EDTA solution till the wine red colour turns blue. (Titre = V_2 ml)

3. Calculate the total hardness in ppm (parts of CaCO_3 per million parts of the water sample).

Calculation :

Strength of standard zinc acetate solution

$$= \frac{w}{0.54846} \text{ (M/100)}$$

\therefore 25 ml of standard zinc acetate $\equiv V_1$ ml of EDTA solution

$$\therefore \text{Strength of EDTA solution} = \left(\frac{25 \times w}{V_1 \times 0.54846} \right) \text{ (M/100)}$$

\therefore 50 ml water sample $\equiv V_2$ ml of EDTA solution

\therefore 1 ml of (M) EDTA solution $\equiv 100$ mg of CaCO_3

$$\therefore V_2 \text{ ml} \left(\frac{25 \times w}{V_1 \times 0.54846} \right) \text{ (M/100) EDTA}$$

$$= \frac{100 \times 25 \times w \times V_2}{V_1 \times 0.54846 \times 100} \text{ mg. of } \text{CaCO}_3$$

$$= \frac{25 w V_2}{0.54846 V_1} \text{ mg of } \text{CaCO}_3$$

\therefore Hardness of water sample

$$\equiv \text{ppm of } \text{CaCO}_3$$

$$= \text{mg. of } \text{CaCO}_3 \text{ per 1000 ml}$$

$$= \frac{25 \times w \times V_2 \times 1000}{V_1 \times 0.54846 \times 50} \text{ mg of } \text{CaCO}_3 \text{ per 1000 ml}$$

$$= \left(\frac{25 \times 1000}{0.54846 \times 50} \right) \times \left(\frac{w V_2}{V_1} \right) \text{ ppm.}$$

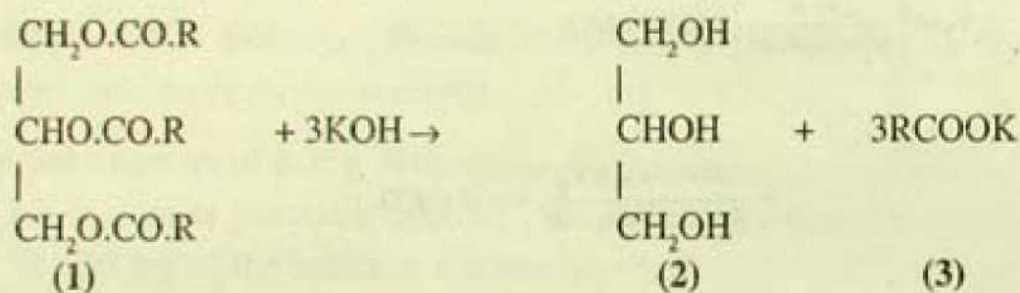
$$= \left(\frac{500}{0.54846} \right) \times \left(\frac{w V_2}{V_1} \right) \text{ ppm.}$$

Experiment No. 2 : Estimation of saponification value of oil / ester/fat.

Oils and fats are glyceryl esters (glycerides) (1) of higher fatty acids. Such esters, which are liquid at 20°C are called *oils*, and those which are solid at 20°C are called *fats*. The glycerides, when refluxed with alcoholic KOH, are hydrolysed to glycerol (2) and the potassium salt of the corresponding higher fatty acids (3). This process of hydrolysis is called *saponification*.

Principle :

Saponification value of an oil/ester is the number of milligrams of KOH required to saponify 1g of oil/fat or ester. A weighed quantity of oil/ester is completely saponified by boiling with a measured excess of standard alcoholic KOH solution. The excess alkali is then back titrated with a standard strong acid (HCl) solution.



1000 ml of (N) HCl solution \equiv 1g-equivalent of KOH \equiv 56.1 g of KOH

or, 1 ml of (N) HCl solution \equiv 1 ml of (N) KOH \equiv 56.1 mg of KOH

Chemicals required :

- Standard (N/20) oxalic acid solution : To be prepared by accurate weighing. ~0.3 g. (w_1) of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ per 100 ml solution. Strength = ($w_1/0.3152$) (N/20)
- Mustard oil
- (~N/2) alcoholic KOH solution : ~ 7.0 g. of KOH per 250 ml solution. Dilute 10 ml of this solution to 100 ml in a 100 ml volumetric flask to have a (~ N/20) KOH solution.
- (~N/2) HCl solution : ~ 10-12 ml of conc. HCl per 250 ml solution. Dilute 10 ml of this solution to 100 ml in a 100 ml volumetric flask to obtain (~ N/20) HCl solution.

Procedure :

- Standardise the alcoholic (~ N/20) KOH solution against standard (~N/20) oxalic acid :

Take an aliquot of 25 ml of the standard (N/20) oxalic acid in a 250 ml conical flask, add 2-3 drops of phenolphthalein indicator, dilute to 50 ml and titrate with the (~ N/20) KOH solution upto a red end point. (Titre = V_1 ml). Calculate the exact strength of the (~N/20) KOH solution and finally that of the (~ N/2) KOH solution.

2. Standardise the (~N/20) HCl solution against the standard ~N/20) KOH solution :

Take an aliquot of 25 ml of the (~N/20) HCl solution in a 250 ml conical flask, add 2-3 drops of phenolphthalein indicator, dilute to 50 ml and titrate with the standard (~N/20) KOH solution up to a red end point. (Titre = V_2 ml). Calculate the exact strength of the (~N/20) HCl solution and finally the exact strength of the (~ N/2) HCl solution.

3. *Estimation of saponification value :*

- (a) Weigh out accurately ~2.0 g (w_2) of the supplied mustard oil in a 250ml conical flask fitted with an air condenser. Add 50 ml of ~N/2) alcoholic KOH solution to it using a burette. Reflux the mixture on a hot water bath till the oil is completely saponified which is indicated by the absence of any oily matter. Allow the mixture to cool to room temperature, add 2-3 drops of phenolphthalein indicator and titrate the unreacted KOH by the standard ~N/2) HCl solution, to a colourless end point (Titre = V_3 ml).
- (b) Run a blank experiment under the same condition using the same quantity (50 ml) of KOH but without using the oil. Titrate the solution with the standard ~N/2) HCl using phenolphthalein indicator upto a colourless end point (Titre = V_4 ml).

$$\therefore \text{KOH consumed by } w_2 \text{ g. of oil/ester} \equiv (V_4 - V_3) \text{ ml of } (\sim N/2) \text{ HCl}$$

4. Calculate the saponication value of the sample of oil/ester.

Calculation :

$$\text{Strength of standard oxalic acid solution} = (w_1/0.3152) (N/20)$$

$$\therefore 25 \text{ ml standard } (w_1/0.3152) (N/20) \text{ oxalic acid}$$

$$\equiv V_1 \text{ ml of } (\sim N/20) \text{ KOH solution.}$$

$$\therefore \text{Exact strength of } (\sim N/2) \text{ KOH solution} = \left(\frac{25 \times w_1}{V_1 \times 0.3152} \right) \left(\frac{N}{2} \right)$$

\therefore 25 ml of ($\sim N/20$) HCl solution

$\equiv V_2$ ml of ($\sim N/20$) KOH solution.

$$\therefore \text{Exact strength of } (\sim N/20) \text{ HCl solution} = \left(\frac{V_2 \cdot w_1}{2 \times 0.3152 \times V_1} \right) (N)$$

\therefore KOH consumed by w_2 g. of oil/ester

$$\begin{aligned} &\equiv (V_4 - V_3) \text{ ml of } \left(\frac{V_2 \cdot w_1}{2 \times 0.3152 \times V_1} \right) (N) \text{ HCl} \\ &\equiv (V_4 - V_3) \text{ ml of } \left(\frac{V_2 \cdot w_1}{2 \times 0.3152 \times V_1} \right) (N) \text{ KOH} \\ &\equiv \frac{(V_4 - V_3) \times V_2 \times w_1}{2 \times 0.3152 \times V_1} \text{ ml of } (N) \text{ KOH} \\ &\equiv \frac{56.1 \times (V_4 - V_3) \times V_2 \times w_1}{2 \times 0.3152 \times V_1} \text{ mg of KOH} \end{aligned}$$

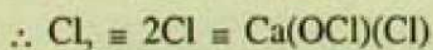
(\because 1 ml of (N) KOH \equiv 56.1 mg of KOH)

$$\begin{aligned} \therefore \text{KOH consumed by 1 g. of oil/ester} &= \frac{56.1 \times w_1 \times (V_4 - V_3) \times V_2}{2 \times 0.3152 \times w_2 \times V_1} \text{ mg.} \\ &= \text{Saponification value of the oil/ester.} \end{aligned}$$

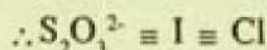
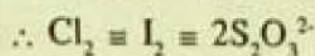
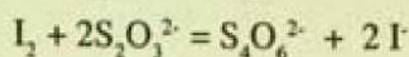
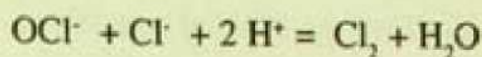
Experiment No. 3 : Estimation of available chlorine in bleaching powder.

Principle :

Available chlorine in bleaching powder refers to the chlorine liberated from it by the action of dilute acids and is expressed by the percentage by weight of bleaching powder.



When an aqueous suspension of bleaching powder is treated with excess of KI solution in presence of dilute acid, iodide is oxidised to iodine by the hypochlorite ion OCl⁻. The liberated iodine is titrated with standard thiosulfate solution using starch indicator. From the titre value of thiosulfate solution, the percentage of the available chlorine may be calculated.



\therefore 1000 ml of (N) thiosulfate solution \equiv 1g. equivalent of chlorine
 \equiv 35.46 g. of chlorine

Chemicals required :

- Standard (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution : To be prepared by accurate weighing.
 If w_1 g. of $\text{K}_2\text{Cr}_2\text{O}_7$ is present in 250 ml solution, then the strength of $\text{K}_2\text{Cr}_2\text{O}_7$ solution = $(w_1/0.6129)$ (N/20)
- (N/20) $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ solution : \sim 3-4 g. per 250 ml.
- 10% KI solution
- 1% Starch solution
- 4(N) H_2SO_4
- Glacial acetic acid.

Procedure :

- Standardisation of sodium thiosulfate solution against standard (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution :*

Take an aliquot of 25 ml of the standard (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution, add 25 ml of 4(N) H_2SO_4 and 10 ml of 10% KI solution. Cover the flask with a clock glass, allow to stand in dark for 2-3 minutes. Dilute to 200 ml with distilled water and titrate with the thiosulfate solution till a light yellow-brown colour appears. Add 2-3 ml of 1% starch solution and continue titration with the thiosulfate solution till the blue colour of the solution is discharged and a bright green colour appears (Titre = V_1 ml).

- Estimation of available chlorine in bleaching powder:*

Weigh out accurately \sim 2.5g (w_2) of bleaching powder in a small glass mortar, add a little distilled water and triturate to make a paste. After settling, transfer the supernatant liquid in to a 250 ml volumetric flask. Repeat the procedure till the whole mass of the sample is transferred to the volumetric flask. Make up the volume up to the mark with distilled water, shake well to mix uniformly.

Take 50 ml of this solution in to a 500ml conical flask using a burette. Add 25 ml of distilled water, 20 ml 10% KI solution and 10 ml glacial acetic acid. Titrate the liberated iodine with standard $\sim(N/20)$ sodium thiosulfate solution using starch indicator to a colourless end point (Titre = V_2).

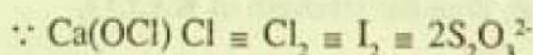
3. Calculate the % of available chlorine in the sample of bleaching powder.

Calculation :

Strength of standard $K_2Cr_2O_7$ solution = $(w_1/0.6129)$ (N/20).

25 ml $K_2Cr_2O_7 \equiv$ Iodine $\equiv V_1$ ml of thiosulfate solution

$$\therefore \text{Strength of thiosulfate solution} = \left(\frac{w_1 \times 25}{0.6129 \times V_1} \right) (N/20)$$



\therefore 1000 ml of (N) thiosulfate \equiv 35.46 g. of Cl.

$$\begin{aligned} \therefore V_2 \text{ ml of } \left(\frac{w_1 \times 25}{0.6129 \times V_1} \right) (N/20) \text{ thiosulfate} \\ \equiv \frac{35.46}{1000} \times V_2 \times \frac{w_1 \times 25}{0.6129 \times V_1 \times 20} \text{ g. of Cl.} \end{aligned}$$

$$\therefore Cl \% = \frac{35.46 \times 25 \times V_2 \times w_1 \times 100}{1000 \times 0.6129 \times V_1 \times w_2 \times 20} \%$$

$$= \left(\frac{35.46}{8 \times 0.6129} \right) \times \left(\frac{V_2}{V_1} \times \frac{w_1}{w_2} \right) \%$$

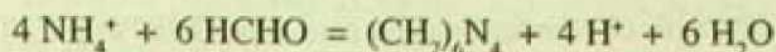
= Available chlorine (%).

Experiment No. 4 : Estimation of NH_4^+ by formol titration.

Principle :

NH_4^+ ion being a very weak acid ($pK_{NH_4^+}^H = 9.2$) can not be quantitatively titrated with strong base such as NaOH using phenolphthalein indicator ($pK_m = 9.6$). Ammonium salts react with neutral formalin solution (HCHO) to produce hexamethylene tetramine

(i.e., hexamine $(\text{CH}_2)_6\text{N}_4$), liberating an equivalent amount of acid (H^+).



$\therefore \text{NH}_4^+ \equiv \text{H}^+ \equiv \text{NaOH} \equiv 1 \text{ equivalent of NaOH}$

$\therefore 1000 \text{ ml of (N) NaOH solution} \equiv 18 \text{ g. of NH}_4^+$

More exactly, the acid, $(\text{CH}_2)_6\text{N}_4\text{H}^+$, corresponding to hexamine is produced in the solution. pK^{H} value of this acid is ~ 5 . So it is a much stronger acid than NH_4^+ ion, and can be titrated with NaOH solution using phenolphthalein indicator.

Chemicals required :

- Standard (N/20) oxalic acid solution : To be prepared by accurate weighing.
- Formalin : 40% aqueous formaldehyde solution : Formalin solution always contains some formic acid (HCOOH , $\text{pK}^{\text{H}} = 3.7$) which is a fairly strong acid than $(\text{CH}_2)_6\text{N}_4\text{H}^+$ and NH_4^+ . Formalin solution is to be neutralised by NaOH solution using the same indicator. The neutralised formalin solution is to be used in the estimation.
- ($\sim \text{N}/20$) NaOH solution : Dissolve $\sim 0.5\text{-}0.6 \text{ g}$ of (A.R.) NaOH in distilled water and dilute to $\sim 250 \text{ ml}$.
- Phenolphthalein indicator : 0.5% solution in 1:1 alcohol.
- 5% NaOH solution
- 1:10 HCl solution

Procedure :

- Standardise the ($\sim \text{N}/20$) NaOH solution against a standard (N/20) oxalic acid solution using phenolphthalein indicators as usual. (cf. Ch-2.) (titre = $V_1 \text{ ml}$)
- Preparation of neutral formalin solution :*

Take 10 ml of commercial formalin solution in a beaker add 25ml distilled water and one drop of phenolphthalein indicators. Neutralise the above solution by adding drops of 5% NaOH solution till the colour of the solution turns red. Then just discharge the red colour by adding drops of (1:10) HCl solution. Add drops of the standard (N/20) NaOH so that the red colour just appears. The formalin solution is just neutral at this stage.

- Estimation of NH_4^+ :*

Pipette out 25ml of the supplied ammonium salt (NH_4Cl) solution into a 250 ml conical flask, add $\sim 25 \text{ ml}$ of the neutralised formalin solution and 2-3 drops of phenolphthalein indicator. Titrate the resulting solution with the standard (N/20) NaOH solution till the solution just assumes a red colour. (titre = $V_2 \text{ ml}$). Repeat the titration to get concordant readings.

4. Calculate the amount of NH_4^+ in the supplied solution in g/L^{-1} .

Strength of standard oxalic acid = $(w/0.7879) (N/20)$

25 ml $(w/0.7879)(N/20)$ oxalic acid $\equiv V_1$ ml NaOH

$$\therefore \text{Strength of NaOH} = \frac{25 \times w}{V_1 \times 0.7879} (N/20)$$

\therefore 1000 ml of (N) NaOH \equiv 18 g. of NH_4^+

25 ml of sample NH_4^+ solution

$$\equiv V_2 \text{ ml} \left(\frac{25 \times w}{V_1 \times 0.7879} \right) (N/20) \text{ NaOH}$$

$$\equiv \frac{18 \times V_2 \times 25 \times w}{1000 \times V_1 \times 0.7879 \times 20} \text{ g. of } \text{NH}_4^+$$

\therefore Strength of the NH_4^+ solution in g. of NH_4^+ per 1000 ml (g./lit)

$$= \left(\frac{18}{0.7879 \times 20} \right) \times \left(\frac{V_2 \times w}{V_1} \right) \text{ g./lit}$$

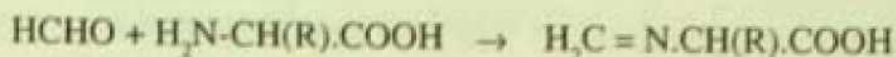
Experiment No. 5 : Estimation of amino acid by formol titration.

Principle :

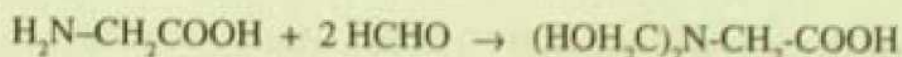
In aqueous solution of an amino acid, $(\text{H}_2\text{NCH(R)COOH})$, the following equilibrium exists :



The dipolar ion (*zwitterion*) structure accounts for the absence of any acidic and basic property of aqueous solution of the amino acid. For this reason amino acids cannot be titrated directly with an alkali. But in the presence of neutralised formalin solution, amino acids behave as strong monoprotic acids and can be quantitatively titrated with standard alkali. Formalin stabilises the amino ($-\text{NH}_2$) group by forming the Schiff base linkage ($-\text{N}=\text{CH}-$), as a result, zwitterion can not be formed and the carboxylate group of the amino acids can be titrated with a strong base (NaOH) using phenolphthalein indicator.



But the reaction is more complex. As for example, formaldehyde reacts with -NH_2 group of glycine to form dimethylol glycine, which behaves as a strong monoprotic acid.



In either way,

$$\begin{aligned} 1000 \text{ ml of (N) NaOH} &\equiv 1 \text{ g. equivalent of glycine} \equiv 75 \text{ g. of glycine} \\ &\equiv 1 \text{ F. W. of amino acid.} \end{aligned}$$

Chemicals required :

- a) Standard $\sim(\text{N}/20)$ oxalic acid solution: To be prepared by accurate weighing.

Weigh out accurately $\sim 0.8 \text{ g}$ (exactly 0.7879 g) of (A.R.) oxalic acid in a 250 ml volumetric flask, dissolve in distilled water and make upto the mark with distilled water. Mix the solution uniformly.

- b) $\sim(\text{N}/20)$ NaOH solution : ~ 0.5 to 0.6 g. of (A.R.) NaOH per 250 ml solution.

- c) Formalin solution : 40% aqueous solution of formaldehyde : To be neutralised with NaOH using phenolphthalein indicator.

Take 10 ml of the formalin solution in a beaker add 25 ml of distilled water and 2 drops of phenolphthalein. Neutralise the free acid with 5% NaOH solution and $1:10$ HCl solution as required and finally with drops of the titrant ($\sim \text{N}/20$) NaOH solution to a just red colour of phenolphthalein.

- d) Phenolphthalein indicator : $(0.4 \sim 0.5)\%$ solution in $1:1$ alcohol.

- e) $\sim(\text{N}/20)$ Amino acid solution : Glycine solution (unknown) : 3.75 g. lit^{-1} , or, dissolve $0.9 \sim 1.0 \text{ g.}$ of glycine in distilled water and dilute to 250 ml in a volumetric flask.

Procedure :

1. Standardise the $\sim(\text{N}/20)$ NaOH solution against standard $(\text{N}/20)$ oxalic acid solution using phenolphthalein as indicator as usual. (cf. Ch-2)
2. Estimation of amino acid :

Pipette out 25 ml of the amino acid solution into a 250 ml conical flask. Add 25 ml of the neutralized formalin solution and 2-3 drops of phenolphthalein indicator. Titrate

the mixture with standard ($\sim N/20$) NaOH solution till the red colour of phenolphthalein just appears. (Titrate slowly near the end point adding the titrant NaOH dropwise with constant shaking).

3. Calculate the total amount of amino acid (say glycine) in the supplied solution in g.lit⁻¹.

Strength of oxalic acid = $(w/0.7879) (N/20)$, where, w = wt. of oxalic acid per 250 ml solution.

If 25 ml oxalic acid $\equiv V_1$ ml of NaOH solution,

$$\text{strength of NaOH solution} = \left[\frac{w \times 25}{0.7879 \times V_1} \right] (N/20)$$

If 25 ml of amino acid (say glycine) solution $\equiv V_2$ ml of NaOH solution,

\therefore 1000 ml of (N) NaOH \equiv 1 F. W. of amino acid \equiv 75 g. of glycine

$\therefore V_2$ ml of $[(w \times 25) / (0.7879 \times V_1)] (N/20)$ NaOH solution

\therefore 1000 ml of sample glycine solution contains

$$= \frac{75 \times w \times V_2}{0.7879 \times V_1 \times 20} \text{ g. of glycine}$$

$$\therefore \text{Strength of glycine solution} = \left(\frac{75}{0.7879 \times 20} \right) \times \left(\frac{w V_2}{V_1} \right) \text{ g. lit}^{-1}.$$

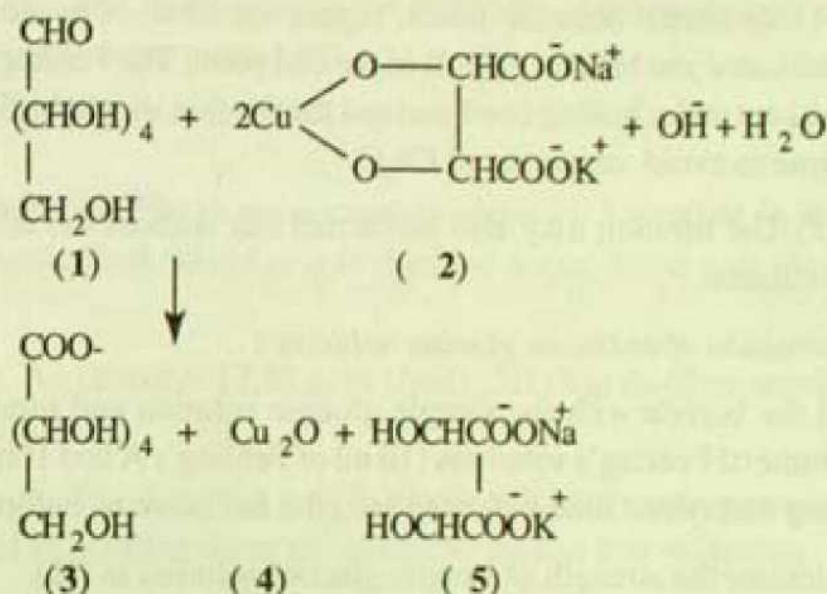
$$\therefore \text{Strength of amino acid solution} = \left(\frac{\text{F.W.}}{0.7879 \times 20} \right) \times \left(\frac{w V_2}{V_1} \right) \text{ g. lit}^{-1}$$

Experiment No. 6 : Estimation of glucose by titration using Fehling's solutions.

Theory :

Glucose (1) is a reducing sugar. Fehlings solution (2) is composed of (i) copper(II) sulfate (Fehling's solution A) and (ii) sodium potassium tartarate (5) rendered strongly alkaline with NaOH (Fehling's solution B). A mixture of equal volumes of these two solutions is the actual reagent.

Under boiling condition, glucose (1) is quantitatively oxidised by Fehling's solution (2) to gluconate (3) with precipitation of red cuprous oxide (4).



The unknown glucose solution may be estimated by titrating a known volume of the Fehling's solution first with a standard glucose solution using methylene blue as indicator and then by titrating the same volume of the Fehling's solution with the unknown glucose solution following the same procedure.

Chemicals required :

- Standard glucose solution : Weigh out accurately ~0.5 g (w) of (A.R.) glucose in a 100 ml volumetric flask, dissolve in distilled water, make upto the mark with distilled water and mix uniformly.
- Fehling's Solution A : Dissolve 17.32g. of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in distilled water, dilute to 250 ml and mix uniformly.
- Fehling's Solution B : Dissolve 86.5 g. of Rochelle salt (sodium potassium tartarate, $\text{Na}^+ \text{OOCCH}(\text{OH})\text{CH}(\text{OH})\text{COO}^-\text{K}^+ \cdot 4\text{H}_2\text{O}$) and 25g. of NaOH in distilled water and dilute the mixture to 250ml with distilled water and mix uniformly.
- Methylene blue indicator : 0.5% aqueous solution.

Procedure:

1. *Standardisation of Fehling's solution :*

Pipette out 10 ml of Fehling's A and 10 ml Fehling's B in a 150ml conical flask. Boil the mixture gently on an asbestos-centered wire-gauge. Add standard glucose solution dropwise from a burette to the gently boiling glucose solution till the supernatant liquid appears pale blue. Add 2-3 drops of methylene blue indicator and continue the titration keeping the solution in the gently boiling condition till the blue colour is just discharged with the simultaneous settling down of a bright red precipitate of cuprous oxide. (Titre = V_1)

Note : (1) To obtain accurate result, repeat the titration by adding the methylene blue indicator just before (~ 2 ml) of the end point. The Fehling's solution should always be kept under boiling condition and the titration should be finished within 2-3 minutes time to avoid oxidation of Cu_2O .

(2) The titration may also be carried out without the addition of methylene blue indicator.

2. *Estimation of unknown glucose solution :*

Fill the burette with the sample glucose solution and titrate a mixture of the same volume of Fehling's solutions (10 ml of Fehling's A and 10ml of Fehling's B mixture) using methylene blue indicator upto the end point as before. (titre = V_2)

1. Calculate the strength of sample glucose solution in (%).

Calculation :

Strength of standard glucose solution = w. g / 100 ml = w %

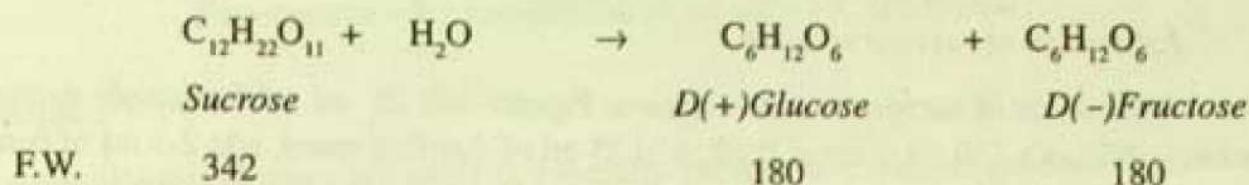
20 ml Fehling's solution $\equiv V_1$ ml of standard glucose solution

$\equiv V_2$ ml of sample glucose solution

$$\therefore \text{Strength of sample glucose solution} = \left(\frac{V_1 \times w}{V_2} \right) \%$$

Experiment No. 7 : Estimation of sucrose by titration using Fehling's solutions

Principle : Sucrose is a non-reducing sugar. It may be estimated by converting it into a mixture of two reducing sugars viz., glucose and fructose (invert sugars) by hydrolysis, effected by boiling with dilute HCl.



\therefore 342 g. of sucrose \rightarrow 360 g. of invert sugar

\therefore 1 g. of invert sugar \equiv (342/360) g. = 0.95 g. of sucrose

The mixture of the invert sugars may be estimated by titrating a known volume of Fehling's solution (equal volumes of Fehling's-A and Fehling's-B) with the sugar mixture using methylene blue as indicator and standardizing the Fehling's solution against a standard glucose solution following the same procedure.

Chemicals required :

- Standard glucose solution: Weigh out accurately about ~ 0.5 g (w) of (A.R.) glucose in a 100 ml volumetric flask, dissolve it in distilled water, dilute upto the mark and mix uniformly.
- Fehling's Solution A: Dissolve 17.32 g. of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in distilled water, dilute to 250 ml and mix uniformly.
- Fehling's Solution B: Dissolve 86.5 g. of Rochelle salt (sodium potassium tartarate) and 25 g. of NaOH in distilled water dilute to 250 ml and mix uniformly.
- Methylene Blue indicator : 0.5% aqueous solution.
- Sample sucrose solution : ~ 0.5% in water. (25 ml ~ 2% sucrose solution on dilution to 100 ml after hydrolytics gives ~ 0.5% solution).

Procedure :

1. Standardisation of Fehling's solution against standard glucose solution :

Pipette out 10 ml each of Fehling's-A and 10ml Fehling's-B in a 150 ml conical flask and add 20 ml distilled water. Boil the mixture gently on an asbestos-centered wire-gauge. Add standard glucose solution dropwise in the gently boiling glucose solution from a burette till the colour of the supernatant liquid appears pale blue. Add 2 to 3 drops of methylene blue indicator and continue the titration with the standard glucose solution keeping the solution in the gently boiling condition till the blue colour is just discharged with simultaneous settling down of a bright red precipitate of cuprous oxide all at once. (titre = V_1). (See also notes 1 and 2 of glucose estimation).

2. Estimation of sucrose solution :

(a) *Hydrolysis of sucrose to invert sugars:* Pipette out 25 ml of the sample sucrose solution (~2%) in a 150 ml conical flask, add 25 ml of distilled water, add 2-3 ml of conc. HCl, heat to 60° - 70°C on a boiling water bath for 15 minutes, when sucrose undergoes hydrolysis to produce equimolar quantities of glucose and fructose. Cool the solution to room temperature and carefully neutralise with powdered Na_2CO_3 avoiding excess. Transfer the solution quantitatively into a 100 ml volumetric flask make up to the mark with distilled water and mix uniformly. This is the invert sugar solution.

(b) *Estimation of invert sugars :* Pipette out 10 ml of each of Fehling's-A and 10ml of Fehling's-B in a 150ml conical flask and add 20ml distilled water. Boil the mixture gently on an asbestos-centered wire gauge, and titrate the mixture with the invert sugar solution till the colour of the supernatant liquid appears pale blue. Add 2-3 drops of methylene blue indicator and continue the titration keeping the solution in the gently boiling condition till the blue colour is just discharged with simultaneous settling down of a bright red precipitate of cuprous oxide all at once. (titre= V_2)

3. Calculate the (%) strength of sample sucrose solution.

Calculation :

Strength of standard glucose solution = $w\%$

20 ml Fehling's solution $\equiv V_1$ ml $w\%$ of glucose solution

$\equiv V_2$ ml of invert sugar solution

$\therefore V_2$ ml of invert sugar $\equiv (w \times V_1 / 100)$ g. of glucose

\therefore 100 ml of invert sugar solution

$$\equiv \frac{w \times V_1 \times 100}{100 \times V_2} \text{ g} \equiv \left(\frac{w \times V_1}{V_2} \right) \text{ g. of glucose.}$$

\equiv 25 ml of sample sucrose solution

$\equiv 0.95 \times [(w \times V_1) / V_2]$ g. of sucrose

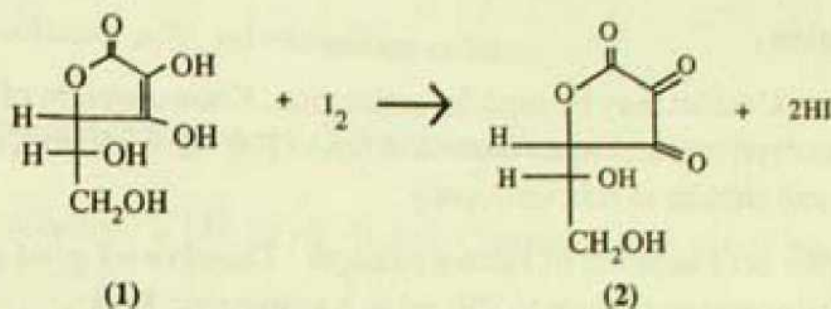
\therefore Total sucrose in 100 ml stock solution = $(0.95 \times 100 / 25) \times [(w \times V_1) / V_2]$ g.

\therefore % Strength of sample sucrose solution = $(4 \times 0.95) \times [(w \times V_1) / V_2] \%$

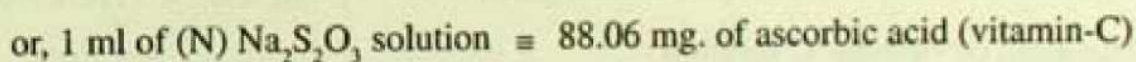
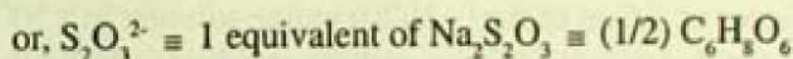
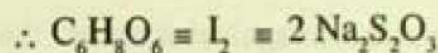
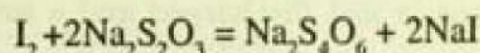
Experiment – 8 : Estimation of vitamin - C (reduced)

Principle :

Vitamin C (ascorbic acid) is generally present as a natural product as reduced *l*-ascorbate. It is a reducing agent. *l*-Ascorbic acid (1) is quantitatively oxidised to dehydro-*l*-ascorbic acid (2) by iodine, which is reduced to hydroiodic acid.



This reaction forms the basis of iodimetric estimation of ascorbic acid. A known volume of an aqueous solution of vitamin C (reduced) is treated with a measured excess of standard iodine solution. After the reaction is over the excess iodine is back titrated with a standard solution of sodium thiosulfate. The difference in the titre of thiosulfate gives the amount of iodine consumed and hence the amount of vitamin C.



Chemical required :

a) Standard (N/20) $K_2Cr_2O_7$ solution (equivalent weight = 49.03):

Weigh out accurately ~ 0.6129 g. (w) of A.R. $K_2Cr_2O_7$ in a 250 ml volumetric flask, dissolve in distilled water, and make up to the mark, and mix uniformly :

$$\therefore \text{Strength} = (w/0.6129) (N/20)$$

- b) ($\sim N/20$) I_2 in KI solution : Dissolve ~ 1.6 g. of iodine in a solution of 2 g. of KI and dissolved in 20 ml of distilled water and dilute to 250 ml with distilled water.
- c) ($\sim N/20$) Thiosulfate solution : Dissolve ~ 3 g. of $Na_2S_2O_3 \cdot 5H_2O$ in distilled water, dilute to ~ 250 ml and mix uniformly.
- d) 10% KI solution.
- e) 1% Starch solution.
- f) Sample solution :
 - (i) Vitamin-C tablet may be used for estimation. Known weight of the tablets may be dissolved in water in a volumetric flask (100 ml or 250 ml), diluted upto the mark and shaken to mix uniformly.
 - (ii) Ascorbic acid solution of known strength : Dissolve ~ 1 g. of ascorbic acid in distilled water and dilute to 250 ml in a volumetric flask.

Procedure :

1. Standardisation of thiosulfate solution against standard ($N/20$) $K_2Cr_2O_7$ solution:

Pipette out 25ml of standard ($N/20$) $K_2Cr_2O_7$ solution in a 500ml conical flask, add 25ml of 4(N) H_2SO_4 , and 10 ml of 10% KI solution, cover the flask and allow to stand in the dark for 2-3 minutes. Dilute with 150 ml of distilled water to adjust the acidity $\sim 0.5N$ and titrate the liberated iodine with the thiosulfate solution till the solution assumes a pale yellow colour. Add 2 ml of 1% starch solution. The solution turns intense blue. Continue the titration till the blue colour is just discharged and a bright green colour appears (titre = V_1 ml).

2. Standardisation of iodine solution against standard thiosulfate solution:

Take an aliquot of 25 ml of the ($\sim N/20$) iodine solution in a 500ml conical flask, dilute to 100 ml with distilled water and titrate with the standard ($\sim N/20$) thiosulfate solution till the solution assumes a pale yellow colour. Add 2 ml of 1% starch solution and continue the titration until the blue colour is just discharged. (titre = V_2 ml).

3. Estimation of vitamin- C solution :

Pipette out 25 ml of the diluted vitamin – C solution in a 500 ml conical flask, dilute with 25 ml of distilled water. Add 1 ml of 4(N) H_2SO_4 to adjust the acidity ≤ 0.1 (N). Add a measured excess (25/50/75 ml say $25 \times x$ ml) of standard ($\sim N/20$) iodine solution using a burette so that the iodine colour persists in the solution, allow to stand for 30 seconds. Add 2 ml of 1% starch indicator, the solution turns blue. Titrate quickly with the standardised ($\sim N/20$) thiosulfate solution till the blue colour is just discharged. (titre = V_3 ml)

3. Calculate total quantity of vitamin- C in the sample.

Calculation :

Strength of standard $K_2Cr_2O_7$ solution = $(w / 0.6129) (N/20)$

25 ml of $(w / 0.6129) (N/20) K_2Cr_2O_7 \equiv$ Iodine $\equiv V_1$ ml thiosulfate solution

\therefore Strength of thiosulfate solution $\equiv (25 \times w) / (V_1 \times 0.6129) (N/20)$

25 ml of Iodine solution $\equiv V_2$ ml thiosulfate solution

$\therefore (25 \times x)$ ml iodine solution $\equiv x \times V_2$ ml thiosulfate solution

$(25 \times x)$ Iodine solution $\equiv (25 \text{ ml of Vitamin C solution} + V_3 \text{ ml of thiosulfate solution})$

$\therefore 25 \text{ ml of Vitamin C solution} \equiv (x \times V_2 - V_3) \text{ ml of thiosulfate solution}$

$\therefore 1 \text{ ml of (N) thiosulfate solution} \equiv 88.06 \text{ mg of Vitamin C}$

$\therefore 25 \text{ ml of vitamin C solution}$

$\equiv (x \times V_2 - V_3) \text{ ml of } (25 \times w) / (V_1 \times 0.6129) (N/20) \text{ thiosulfate solution}$

$$\equiv \frac{88.06 \times (x \times V_2 - V_3) \times 25 \times w}{V_1 \times 0.6129 \times 20} \text{ mg. of vitamin C}$$

$\therefore 1 \text{ ml of Vitamin C solution}$

$$\equiv \frac{88.06 \times (x \times V_2 - V_3) \times 25 \times w}{V_1 \times 0.6129 \times 20 \times 25} \text{ mg. of vitamin C}$$

\therefore Strength of Vitamin C solution

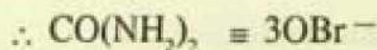
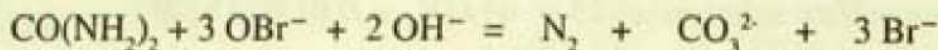
$$= \left(\frac{88.06 \times 1000}{0.6129 \times 20} \right) \times \left(\frac{x V_2 - V_3}{V_1} \right) \text{ mg.lit}^{-1}.$$

$$= \left(\frac{88.06 \times 100}{0.6129 \times 20} \right) \times \left(\frac{x V_2 - V_3}{V_1} \right) \text{ mg.}\%$$

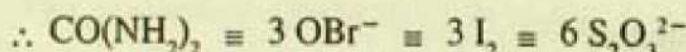
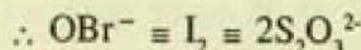
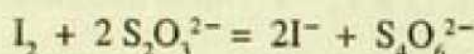
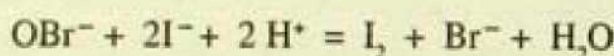
Experiment No. 9 : Estimation of urea by hypobromite method.

Principle :

Urea, $(\text{H}_2\text{NCONH}_2)$, is quantitatively oxidised to liberate nitrogen gas when it is treated with a measured excess of standardised alkaline solution of hypobromite (OBr^-) :



Unreacted hypobromite may be estimated by allowing it to react with an excess of KI in presence of dil. H_2SO_4 , when I_2 is liberated. The liberated I_2 is then back titrated with standard thiosulfate solution using starch as indicator.



or, $\text{S}_2\text{O}_3^{2-} \equiv 1$ equivalent of $\text{Na}_2\text{S}_2\text{O}_3 \equiv (1/6) \text{CO}(\text{NH}_2)_2 \equiv \left(\frac{60}{6}\right)$ g. of urea

$\therefore 1000 \text{ ml of (N) } \text{S}_2\text{O}_3^{2-} \text{ solution} \equiv 10 \text{ g. of urea}$

Hypobromite is unstable when prepared directly from bromine and alkali. It is conveniently produced *in situ* by adding an excess of bromide to a solution of hypochlorite.



Chemicals required :

(a) Standard ((N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution : To be prepared by accurate weighing. Weight out ~ 0.6-0.7 g (w) of A.R. $\text{K}_2\text{Cr}_2\text{O}_7$ in a 250 ml volumetric flask, dissolve in distilled water,

make upto the mark and mix uniformly. Strength = $\left(\frac{w}{0.6129}\right) (\text{N}/20)$

b) (~N/20) thiosulfate solution : Dissolve ~ 3 g. of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in distilled water and dilute to 250 ml, mix uniformly.

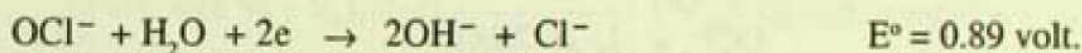
- c) (~N/20) Calcium hypochlorite solution.
- d) KBr
- e) KI
- f) 1% Starch solution
- g) Sample urea solution : ~ 0.5 to 1.0 g. lit⁻¹ in distilled water.

Procedure :

1. (a). Preparation of (~N/20) calcium hypochlorite solution

Depending upon the amount of available chlorine, take 1-2 g. of commercial sample of calcium hypochlorite (bleaching powder) and 100 ml of distilled water in a 250 ml conical flask and shake thoroughly. Filter the slurry through a Whatman No. 1 filter paper to remove iron oxide, excess of calcium hydroxide and any other insoluble material in the commercial product. Dilute the filtrate to 250 ml with distilled water. Formation of turbidity on standing due to the precipitation of calcium carbonate, is of no consequence. The standard solution of hypochlorite should be preserved in dark coloured glass stoppered bottle protected from light.

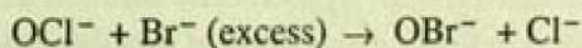
Hypochlorite is a powerful oxidising agent in neutral or alkaline medium.



∴ (OCl⁻/2) = 1 equivalent of OCl⁻

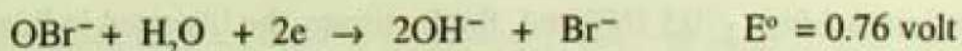
(b) (~ N/20) hypobromite solution :

A hypobromite solution of known concentration may be prepared extemporaneously by adding an excess potassium bromide to a standard solution of hypochlorite :



∴ OBr⁻ ≡ OCl⁻

Hypobromite is also a powerful oxidising agent in neutral or alkaline medium.



∴ (OBr⁻/2) = 1 equivalent of OBr⁻

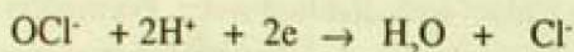
In many cases hypobromite reacts much faster than hypochlorite.

2. *Standardisation of thiosulfate solution :*

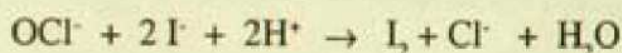
Take an aliquot of 25 ml of standard (N/20) $K_2Cr_2O_7$ in a 500 ml conical flask, add 25 ml of 4(N) H_2SO_4 and 2 g. of KI. Cover the flask and keep in dark for 2-3 minutes. Dilute to 200 ml with distilled water and titrate with the (\sim N/20) thiosulfate solution till a pale yellow (straw) colour appears in the solution. Add 2 ml of starch indicator, the solution turns deep blue. Continue titration with the thiosulfate solution till the blue colour is discharged and a bright green colour appears. (Titre = V_1).

3. *Standardisation of hypochlorite solution :*

Take an aliquot of 25 ml of the (\sim N/20) hypochlorite solution in a 500 ml conical flask, add 25 ml of 4(N) H_2SO_4 and 2 g. of KI. Cover the flask and keep the solution in dark for 2-3 minutes. Dilute to 200 ml with distilled water, titrate with the standard (\sim N/20) thiosulfate solution till a pale yellow (straw) colour appears in the solution. Add 2 ml of starch indicator, the solution turns deep blue. Continue titration with the thiosulfate solution till the blue colour is just discharged (Titre = V_2).



$$\therefore (OCl^- / 2) = 1 \text{ equivalent of } OCl^-$$



$$\therefore (S_2O_3^{2-}) \equiv I \equiv (OCl^- / 2)$$

$$\therefore 1000 \text{ ml of (N) } S_2O_3^{2-} \equiv 1000 \text{ ml of (N) } OCl^-$$

4. *Estimation of urea :*

Take an aliquot of 25 ml of the sample urea solution in a 500 ml conical flask. Add 2 g. of KBr and 0.5 g. of $NaHCO_3$ and shake to dissolve the salts. Add a measured excess (25/50/75 ml or $25 \times x$ ml) of the standard (N/20) hypochlorite solution using a burette till a permanent yellow colour, (due to Br_2) indicating an excess of hypobromite, persists in the solution. Cover the flask and allow to stand for 5 minutes.

Add 10 ml of 6(N) H_2SO_4 (slowly to avoid vigorous effervescence) and then 1 g. of KI. Cover the flask and allow to stand in dark for 2-3 minutes. Dilute to 200 ml with distilled water (to adjust acidity ≤ 0.5 (N)) and finally titrate the liberated iodine with the standard (\sim N/20) thiosulfate solution till a straw (pale yellow) colour appears. Add 2 ml of starch indicator, the solution becomes deep blue. Continue titration with the thiosulfate solution till the blue colour is just discharged (Titre = V_3).

5. Calculate the total quantity of urea present in the sample.

Calculation :

$$\text{Strength of standard } K_2Cr_2O_7 \text{ solution} = \left(\frac{w}{0.6129} \right) \left(\frac{N}{20} \right)$$

$$\begin{aligned} \therefore 25 \text{ ml of standard } \left(\frac{w}{0.6129} \right) \left(\frac{N}{20} \right) K_2Cr_2O_7 \\ \equiv V_1 \text{ ml of thiosulfate solution} \end{aligned}$$

$$\therefore \text{Strength of thiosulfate solution} = \left(\frac{w \times 25}{0.6129 \times V_1} \right) \left(\frac{N}{20} \right)$$

$$\therefore 25 \text{ ml of hypochlorite solution} = V_2 \text{ ml of thiosulfate solution}$$

$$\begin{aligned} \therefore (25 \times x) \text{ ml of hypochlorite solution} \\ \equiv x \cdot V_2 \text{ ml of thiosulfate solution} \end{aligned}$$

$$\text{Excess hypochlorite} \equiv V_3 \text{ ml of thiosulfate solution}$$

$$\therefore \text{Hypochlorite (i.e., hypobromite) consumed by 25 ml urea solution}$$

$$\equiv (x \cdot V_2 - V_3) \text{ ml of } \left(\frac{w \times 25}{0.6129 \times V_1} \right) \left(\frac{N}{20} \right) \text{ thiosulfate solution}$$

$$\therefore 1000 \text{ ml of (N) thiosulfate} \equiv 10 \text{ g. of urea}$$

$$\therefore (x \cdot V_2 - V_3) \text{ ml of } \left(\frac{w \times 25}{0.6129 \times V_1} \right) \left(\frac{N}{20} \right) \text{ thiosulfate}$$

$$\equiv \frac{10 \times 25 w}{1000 \times 0.6129 \times 20} \times \left(\frac{x \cdot V_2 - V_3}{V_1} \right) \text{ g. of urea ,}$$

$$\equiv 25 \text{ ml of sample urea solution}$$

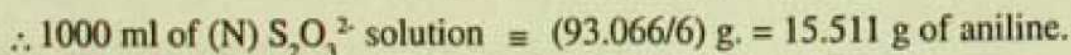
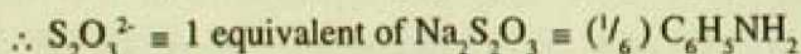
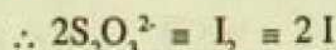
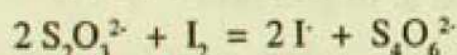
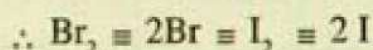
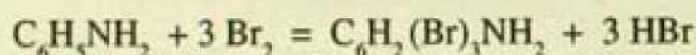
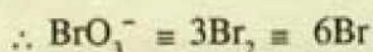
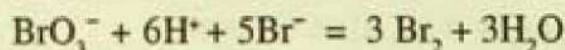
$$\therefore \text{Strength of urea solution} = \frac{10 \cdot w}{0.6129 \times 20} \left(\frac{x \cdot V_2 - V_3}{V_1} \right) \text{ g. lit}^{-1}$$

$$= 0.8158 \times \left(\frac{x \cdot V_2 - V_3}{V_1} \right) \text{ g. lit}^{-1}$$

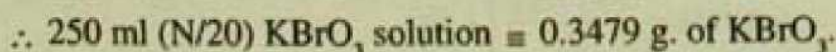
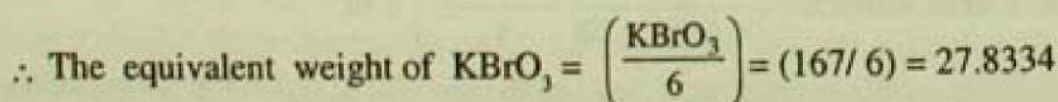
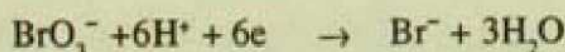
Experiment No. 10 : Estimation of aromatic amines (aniline) by bromination method.

Principle :

Aromatic amines may be estimated by bromination method by treating a known volume of the amine solution in dilute HCl with a measured excess of standard KBrO_3 - KBr mixture (brominating agent). Bromine generated *in situ* by the reaction of BrO_3^- with Br^- in acid medium reacts quantitatively with the amine to form the corresponding bromo derivatives which precipitate. When aniline, $\text{C}_6\text{H}_5\text{NH}_2$, is treated with a measured excess of bromate-bromide mixture in dil. HCl medium, 2,4, 6-tribromoaniline ($\text{C}_6\text{H}_2(\text{Br})_3\text{NH}_2$) is quantitatively formed and precipitated. The unreacted bromine is then made to react with an excess KI and the I_2 that is liberated is titrated with a standard sodium thiosulfate solution using starch indicator. The thiosulfate solution is standardised against the same standard KBrO_3 - KBr mixture. The difference of these two titre values gives the amount of bromine reacted with the amine (aniline) and thus the amine (aniline) is estimated.



In acid solution, BrO_3^- acts as an oxidant according to,



Chemicals required :

- Aromatic amine (aniline) : Stock solution may be prepared by dissolving 3.5 – 4 g (3-4 ml) of freshly distilled aniline in 150 ml of 1:1 HCl solution and finally diluting to one litre with distilled water (acidity ~ 0.8 – 0.9 N).
20-25 ml of this stock solution may be diluted to 100 ml in a volumetric flask. 25 ml of this diluted solution may be used for titration. (acidity ~ 0.2 N).
- Standard (N/20) KBrO_3 – KBr mixture : Weigh out accurately ~ 0.4 g. (w) of (A.R.) KBrO_3 (exactly; 0.3479 g) and add ~ 5 g. of (A.R.) KBr in a 250 ml volumetric flask, dissolve in distilled water and dilute upto the mark with distilled water. Strength : (w/0.3479) (N/20).
- 10% KI solution :
- (N/20) Sodium thiosulfate solution : Dissolve ~ 3-4 g. of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in distilled water and dilute to 250 ml.
- 1% Starch solution :

Procedure :

1. Standardisation of sodium thiosulfate solution against standard KBrO_3 - KBr mixture :

Pipette out 25 ml of standard (N/20) KBrO_3 – KBr mixture in a 500ml conical flask. Add 10 ml of 10% KI solution and then 5 ml of concentrated (A.R.) HCl to adjust the acidity of the resulting solution to ~1.5 N. Cover the flask and keep in dark for 2-3 minutes. Dilute with 100 ml of water to lower the acidity below ~0.5N. Titrate the liberated I_2 with the (~ N/20) thiosulfate till the colour of the solution turns pale yellow (straw colour). Add 2 ml of starch indicator, the solution becomes intense blue. Continue titration with the thiosulfate solution till the blue colour is just discharged. (titre = V_1).

2. Estimation of amine (aniline) :

Transfer the sample amine solution into a 100 ml volumetric flask and make up to the mark with distilled water.

Take an aliquot of 25 ml of the diluted amine solution in to a 500ml conical flask using a burette. Add 10-12 ml concentrated HCl to maintain 1.5 (N) acidity during the subsequent reaction. Add a measured excess (25/50/75 ml say $25 \times x$) ml) of standard (N/20) KBrO_3 – KBr mixture, till a permanent yellow colour due to free Br_2 (indicating an excess of the BrO^- - Br^-), persists in the solution. Cover the flask with a watch glass, shake and allow to stand at room temperature in the dark for 5-10 minutes with occasional shaking. Add 10ml of 10% KI solution, dilute with 150 ml of distilled water to adjust the acidity ~0.5N. Titrate the liberated I_2 with standard (N/20) thiosulfate solution as usual using starch

indicator near the end point. Continue titration till the blue colour is discharged completely. (Shake thoroughly to disorbe any I_2 adsorbed by the precipitate of the bromo derivative). (titre = V_2 ml).

3. Calculate the total quantity of aniline (amine) present in the sample solution.

Calculation :

$$\text{Strength of } KBrO_3 - KBr \text{ mixture} = \left(\frac{w}{0.3479} \right) \left(\frac{N}{20} \right)$$

25 ml of $KBrO_3 - KBr$ mixture $\equiv V_1$ ml thiosulfate solution

$$\therefore \text{Strength of thiosulfate solution} = \left(\frac{25w}{0.3479 \times V_1} \right) \left(\frac{N}{20} \right)$$

$\therefore (25 \times x)$ ml of $KBrO_3 - KBr$ mixture = $x V_1$ ml of thiosulfate solution.

$\therefore KBrO_3 - KBr$ mixture consumed by 25 ml of aniline solution

$$\equiv (V_1 x - V_2) \text{ ml of } \left(\frac{25.w}{0.3479 \times V_1} \right) \left(\frac{N}{20} \right) \text{ thiosulfate solution}$$

$$\equiv \frac{25.w(V_1 x - V_2)}{0.3479 \times V_1 \times 20} \text{ ml of } (N) \text{ thiosulfate solution}$$

$$\equiv \left(\frac{0.01551 \times 25}{0.3479 \times 20} \right) \left(\frac{w(V_1 x - V_2)}{V_1} \right) \text{ g. of aniline}$$

(\therefore 1000 ml of (N) thiosulphate solution \equiv 15.511 g. of aniline.)

\therefore Amount of aniline in the sample solution

$$\equiv \left(\frac{0.015511 \times 25 \times 100}{0.3479 \times 20 \times 25} \right) \times \left[\frac{w(V_1 x - V_2)}{V_1} \right] \text{ g.}$$

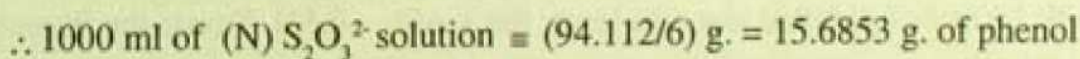
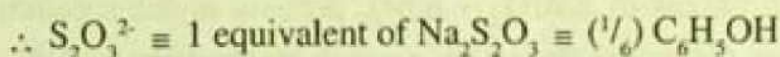
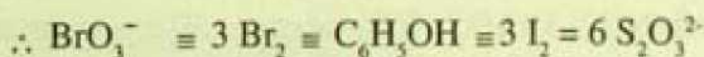
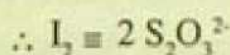
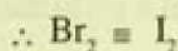
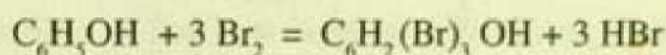
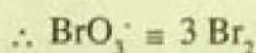
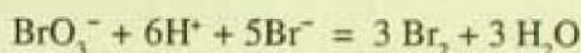
$$\equiv \left(\frac{0.015511 \times 5}{0.3479} \right) \times \left[\frac{w(V_1 x - V_2)}{V_1} \right] \text{ g.}$$

$$= 0.2229 \times \left[\frac{w(V_1 x - V_2)}{V_1} \right] \text{ g.}$$

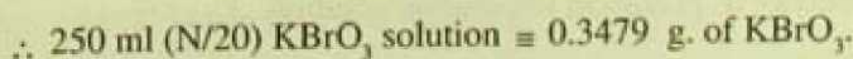
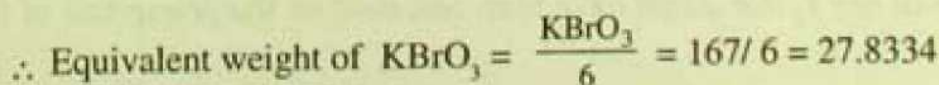
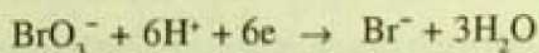
Experiment No. 11 : Estimation of phenol by bromination method.

Principle :

Phenol (C_6H_5OH) may be estimated by bromination method by treating a known volume of the phenol solution with a measured excess of standard $KBrO_3$ - KBr mixture (brominating agent) in presence of dilute acid. Bromine generated *in situ* by the reaction of BrO_3^- with Br^- in acid medium, reacts quantitatively with phenol, to produce 2,4,6- tribromo phenol, $[C_6H_2Br_3(OH)]$ which is precipitated. The unreacted bromine is then made to react with an excess KI , when I_2 is liberated, which is titrated with standard sodium thiosulfate solution using starch as indicator. Thiosulfate solution is standardised against the same standard $KBrO_3$ - KBr mixture. The difference of these two titre values gives the amount of bromine reacted with phenol and thus phenol is estimated.



In acid solution BrO_3^- acts as an oxidising agent according to,



Chemicals required :

- Standard (N/20) $\text{KBrO}_3 - \text{KBr}$ solution.
- 10% KI solution.
- 1% Starch solution.
- (N/20) sodium thiosulfate solution : 3-4 g. of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ per 250 ml solution.
- Sample phenol solution : A stock solution of phenol may be prepared by dissolving ~ 4 g. of phenol in distilled water and diluting to one litre. 20-25 ml of this stock solution may be diluted to 100 ml in a volumetric flask and 25 ml of this diluted solution may be used for titration.

Procedure :

- Standardisation of sodium thiosulfate solution against standard (N/20) $\text{KBrO}_3 - \text{KBr}$ mixture.* Follow the same procedure as in the case of aniline estimation (cf. Experiment 10)
- Estimation of phenol solution :*

Transfer a sample quantity of phenol solution (**Caution, Corrosive**) quantitatively into a 100 ml volumetric flask and make up to the mark with distilled water.

Take an aliquot 25 ml of the diluted phenol solution in to a 500 ml conical flask using a burette. Add 10 ml of concentrated (A.R.) HCl to adjust the acidity of the resulting solution to ~1.5(N) at the time of reaction. Add a measured excess (25/50/75 ml say $(25 \times x)$ ml) of the standard (N/20) $\text{KBrO}_3 - \text{KBr}$ mixture, till a permanent yellow colour due to Br_2 (indicating an excess of $\text{KBrO}_3 - \text{KBr}$), persists in the solution and 2,4,6 tribromo phenol precipitates. Cover the flask with a watch glass, shake and allow to stand in dark at room temperature for 10 minutes with occasional shaking. Add 10ml of 10% KI solution, dilute with 150 ml of distilled water to lower the acidity ~0.5N. Titrate the liberated I_2 with standard (N/20) sodium thiosulfate solution till the solution assumes a pale yellow (straw) colour. Add 2 ml of starch indicator. The solution becomes intense blue. Continue titration with the thiosulfate solution till the blue colour is discharged completely. (Shake the mixture thoroughly to disorb any I_2 that might have been adsorbed on the precipitate of the bromo derivative).

- Calculate total quantity of phenol in the sample solution.

Calculation :

Let w.g. of KBrO_3 is dissolved in 250 ml solution.

$$\therefore \text{Strength of } \text{KBrO}_3 - \text{KBr mixture} = \left(\frac{w}{0.3479} \right) (N/20)$$

\therefore 25 ml of $\text{KBrO}_3 - \text{KBr mixture} \equiv V_1$ ml of thiosulfate solution

$$\therefore \text{Strength of thiosulfate solution} = \left(\frac{25.w}{0.3479 \times V_1} \right) (N/20)$$

$\therefore (25 \times x)$ ml of $\text{KBrO}_3 - \text{KBr mixture} \equiv V_1 \cdot x$ ml of thiosulfate solution

$\therefore \text{KBrO}_3 - \text{KBr mixture consumed by 25 ml of phenol solution}$

$$\equiv (V_1 x - V_2) \text{ ml of } \left(\frac{25.w}{0.3479 \times V_1} \right) (N/20) \text{ thiosulfate solution}$$

$$\equiv \frac{25.w(V_1 x - V_2)}{0.3479 \times V_1 \times 20} \text{ ml of (N) thiosulfate solution}$$

$$\equiv \left(\frac{0.0156853 \times 25}{0.3479 \times 20} \right) \frac{w(V_1 x - V_2)}{V_1} \text{ g. of phenol}$$

(\therefore 1000 ml of (N) thiosulfate solution \equiv 15.6853 g. of phenol.)

\therefore Amount of phenol in the unknown solution

$$= \left(\frac{0.0156853 \times 25 \times 100}{0.3479 \times 20 \times 25} \right) \times \left[\frac{w(V_1 x - V_2)}{V_1} \right] \text{ g.}$$

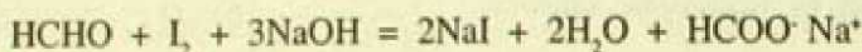
$$= \left(\frac{0.0156853 \times 5}{0.3479} \right) \times \left[\frac{w(V_1 x - V_2)}{V_1} \right] \text{ g.}$$

$$= 0.2254 \times [w(V_1 x - V_2) / V_1] \text{ g.}$$

Experiment No. 12 : Estimation of formaldehyde (formalin)

Principle :

Formaldehyde (formalin), HCHO , is estimated by iodimetric method. When a known volume of formalin solution is allowed to react with a measured excess of iodine (I_2) solution in weakly alkaline medium, formaldehyde is quantitatively oxidised to formate (HCOO^-) ion according to,



$$\therefore \text{I}_2 = \text{HCHO}$$

By back titrating the excess iodine with a standard solution of sodium thiosulfate in weakly acidic medium, it is possible to determine the quantity of I_2 that has reacted with HCHO , hence the quantity of HCHO present in the formalin solution can be found out from the difference in the titre values. Thiosulfate ($\text{S}_2\text{O}_3^{2-}$) is oxidised by I_2 to tetrathionate ($\text{S}_4\text{O}_6^{2-}$) according to,



$$\therefore \text{I}_2 = 2\text{S}_2\text{O}_3^{2-}$$

$$\therefore 2\text{S}_2\text{O}_3^{2-} = \text{I}_2 = \text{HCHO}$$

$$\therefore 2000 \text{ ml of (N) thiosulfate} = 30 \text{ g. of HCHO}$$

$$\therefore 1 \text{ ml of (N) thiosulfate} = (30/2000) \text{ g.} = 0.015 \text{ g. of HCHO.}$$

Chemicals required :

1. $\text{K}_2\text{Cr}_2\text{O}_7$ (A.R.).
2. Sodium thiosulfate solution.
3. (~ N/20) Iodine solution (100 ml). Dissolve 2 g. of iodate free potassium iodide in 20 ml of distilled water taken in a stoppered 250 ml conical flask. Transfer 0.6 – 0.8 g of resublimed iodine in to it and shake well to dissolve completely. Cool to room temperature and dilute to 100 ml with distilled water.
4. 5% NaOH solution (~ 1.25 N) 100 ml
5. (i) 4(N) HCl solution 100 ml
(ii) 5% HCl solution (~ 0.5 N) 100 ml
6. Starch indicator solution.

Procedure :

1. Prepare 25 ml of a standard (N/20) $K_2Cr_2O_7$ by accurate weighing ($\sim 0.6 - 0.8$ g/ 250 ml)
2. Prepare 200 ml of (\sim N/20) sodium thiosulfate solution.
3. Standardise the sodium thiosulfate solution against standard (N/20) $K_2Cr_2O_7$ solution.

Take an aliquot of 25 ml of standard (N/20) $K_2Cr_2O_7$ solution in a 500 ml conical flask, add 25 ml of 4(N) HCl, 2 g. of KI, stopper the flask and allow to stand in dark for $\sim 2 - 3$ minutes. Dilute with 150 ml of distilled water to adjust the acidity to $\leq 0.5(N)$ and titrate with the (\sim N/20) thiosulfate solution as usual using starch indicator near the end point. Colour change at the end point is from blue to bright green (titre = V_1 ml).

4. Standardization of I_2 solution.

Take an aliquot of 25 ml of the I_2 solution in a 500 ml conical flask, add 25 ml of the 5% HCl solution and titrate with standard (N/20) thiosulfate solution using starch indicator as usual. Colour change at the end point is from blue to colourless. (titre = V_2 ml)

5. Estimation of formalin :

- (a) Transfer quantitatively a known volume (V ml) of the sample formalin solution into a 100 ml volumetric flask and make up to the mark with distilled water and mix uniformly.
- (b) Take an aliquot of 25 ml of the diluted solution of formalin into a 500 ml conical flask, add a measured excess (25 / 50 / 75 ml i.e., $25 \times x$ ml, as required) of standard (N/20) I_2 solution and drops of 5% NaOH solution till the solution becomes light yellow and the yellow colour persists even the mixture is kept for 15 minutes. Yellow colour may disappear if the NaOH solution is added in excess.

After standing for 15 minutes add 15 ml of 5% HCl solution and titrate the liberated I_2 with standard (N/20) thiosulfate solution using starch indicator as usual. Colour change at the end point is from blue to colourless. (titre = V_3 ml)

6. Calculate the % of HCHO in sample formalin solution.

Calculation :

$$\text{Strength } K_2Cr_2O_7 \text{ solution} = \frac{w}{0.6129} (N/20)$$

where, w = wt. of $K_2Cr_2O_7$ in 250 ml solution.

25 ml of standard ($w / 0.6129$) (N/20) $K_2Cr_2O_7$ = V_1 ml of thiosulfate solution.

$$\therefore \text{Strength of thiosulfate solution} = \left(\frac{25 \times w}{V_1 \times 0.6129} \right) (N/20)$$

25 ml of I_2 solution $\equiv V_2$ ml of thiosulfate solution

$\therefore (25 \times x)$ ml of I_2 solution

$$\equiv (V_2 \times x) \text{ ml of thiosulfate solution}$$

$$\equiv V_3 \text{ ml of thiosulfate solution} + 25 \text{ ml of diluted formalin solution.}$$

\therefore 25 ml of sample of diluted formalin solution

$$\equiv (V_2 x - V_3) \text{ ml of } \left(\frac{25 \times w}{V_1 \times 0.6129} \right) (N/20) \text{ thiosulfate solution.}$$

$$\equiv \left(\frac{25}{0.6129 \times 20} \right) \times \frac{w (V_2 x - V_3)}{V_1} \text{ ml of (N) thiosulfate solution.}$$

$$\equiv \left(\frac{25 \times 0.015}{0.6129 \times 20} \right) \times \frac{w (V_2 x - V_3)}{V_1} \text{ g of HCHO}$$

\therefore Total formaldehyde in 100 ml of the diluted formalin solution

$$\equiv \left(\frac{25 \times 0.015 \times 100}{0.6129 \times 20 \times 25} \right) \times \frac{w (V_2 x - V_3)}{V_1} \text{ g of HCHO in V ml of the sample}$$

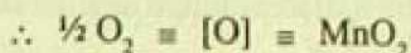
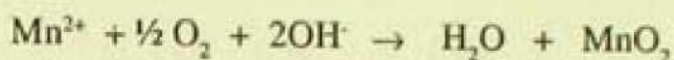
$$= 0.1224 \times \frac{w (V_2 x - V_3)}{V_1} \text{ g. of HCHO}$$

\therefore Strength of the sample formalin solution $= 12.24 \times [w (V_2 x - V_3) / V_1 V_1] \%$.

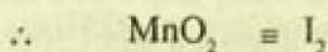
Experiment No. 13 : Estimation of dissolved oxygen in water samples

Principle :

Dissolved oxygen (D.O.) in water samples may be conveniently determined by *Winkler's iodometric method*. A known volume of water sample containing D.O. is allowed to react with sufficient excess of iodide (I^-) in alkaline medium in the presence of Mn^{II} -salt ($MnSO_4$), which is first oxidised by dissolved oxygen, when MnO_2 is precipitated according to



When the reaction mixture is acidified with dilute H_2SO_4 (never HCl), the precipitated MnO_2 in acid medium oxidises I^- to liberate an equivalent amount of iodine (I_2) according to,



The liberated I_2 may then be estimated by titrating with a standard solution of sodium thiosulfate ($S_2O_3^{2-}$), which is oxidised by I_2 to tetrathionate ($S_4O_6^{2-}$) according to,



Therefore, $2S_2O_3^{2-} \equiv I_2 \equiv MnO_2 \equiv \frac{1}{2} O_2 \equiv [O]$.

\therefore 2000 ml of (N) $S_2O_3^{2-} \equiv 8$ g. of oxygen.

Chemicals required

All the solutions are to be prepared in recently boiled distilled water cooled to room temperature in stoppered container to avoid contamination from D.O. in distilled water.

1. Standard (N/20) $K_2Cr_2O_7$ solution : To be prepared by accurate weighing ($\sim 0.6 - 0.8$ g), (say, w.g.) per 250 ml. Strength = $(w/0.6129)$ (N/20).
2. (\sim N/20) Sodium thiosulfate solution : Dissolve $\sim 3-4$ g. of $Na_2S_2O_3 \cdot 5H_2O$ in ~ 200 ml of water and mix uniformly.

3. 40% KF or NaF solution : Dissolve ~ 4 g. of the salt in ~ 10 ml of water.
4. 36% MnSO_4 solution : Dissolve ~ 4-5 g. of (A.R.) $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ or $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ in ~ 10 ml of water.
5. Alkaline Iodide Azide solution : Dissolve ~ 5 g. of (A.R.) NaOH, ~ 1-2 g. of NaI or KI and ~ 0.2 – 0.5 g. of NaN_3 in water and dilute to 100 ml.
6. 9(N) H_2SO_4 solution : (1 : 4) H_2SO_4 : water ~ 100 ml.
7. Starch indicator solution.

Procedure :

1. Standardise the (~ N/20) sodium thiosulfate solution against standard (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ using starch indicator as usual.

[Note : Acidity of the medium should be ~ 2(N) for iodine liberation by $\text{K}_2\text{Cr}_2\text{O}_7$ from KI or NaI, and $\leq 0.5(\text{N})$ for titration of I_2 with thiosulfate]

2. Dilute exactly 50 ml of the (~ N/20) thiosulfate solution with distilled water in a 100 ml volumetric flask to obtain at (~ N/40) thiosulfate solution.
3. Take an aliquot of 100 ml of the sample water into a 500 conical flask add 2 ml of 40% KF (or NaF) solution (to mask Fe^{3+} if any), 2 ml of 36% MnSO_4 solution and 2 ml of the alkaline-iodide azide mixture. Shake well to mix uniformly and allow the precipitate (of MnO_2) to settle down. Add 8 ml of 9(N) H_2SO_4 and shake the mixture thoroughly to dissolve the precipitate completely while cooling to room temperature. Add a few more drops of the 9(N) H_2SO_4 solution if necessary, stopper the flask, allow to stand for 2 – 3 minutes in dark. Dilute the mixture with ~ 80 ml of distilled water and titrate the liberated I_2 with the standard (N/40) sodium thiosulfate solution using starch indicator as usual. Colour change at the end point will be from blue to colourless. Record the titre.
4. Calculate the amount of D.O. in mg. lit^{-1} .

Calculation :

Strength of standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution = $(w/0.6129) (\text{N}/20)$

where, w = wt. of $\text{K}_2\text{Cr}_2\text{O}_7$ per 250 ml solution.

If 25 ml standard (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$

$\equiv V_1$ ml of thiosulfate solution

then, strength of thiosulfate solution

$$= \left(\frac{25 \times w}{V_1 \times 0.6129} \right) (\text{N}/20)$$

∴ Actual strength of titrant thiosulfate solution

$$= \left(\frac{25 \times w}{V_1 \times 0.6129} \right) (N/40)$$

If D.O. in 100 ml of water sample

$$\equiv V_2 \text{ ml of } \left(\frac{25 \times w}{V_1 \times 0.6129} \right) (N/40) \text{ thiosulfate solution}$$

$$\equiv \left(\frac{25}{0.6129 \times 40} \right) \times \left(\frac{wV_2}{V_1} \right) \text{ ml of (N) thiosulfate solution}$$

$$\equiv \left(\frac{25 \times 8}{2000 \times 0.6129 \times 40} \right) \times \left(\frac{wV_2}{V_1} \right) \text{ g. of oxygen}$$

$$= 4.08 \times \left(\frac{wV_2}{V_1} \right) \text{ mg of oxygen}$$

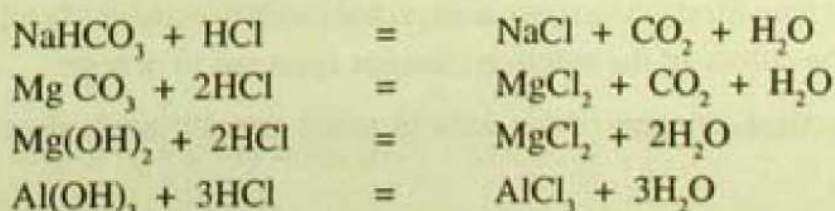
$$\therefore \text{D.O. in mg/litre} = 40.8 \times \left(\frac{wV_2}{V_1} \right)$$

Experiment No. 14 : Determination of alkali content of antacid tablets using HCl

Principle :

Active ingredients of common antacid tablets are weakly basic substances, viz., sodium bicarbonate, magnesium hydroxide, magnesium carbonate, aluminium hydroxide etc. Except sodium bicarbonate, the others are sparingly soluble in water. Moreover, aluminium hydroxide is amphoteric in nature.

For the determination of alkali content of an antacid tablet, it is therefore convenient to dissolve a known weight of the tablet sample in a measured excess of standard HCl solution and then estimation of the unreacted acid by titration with a standard solution of NaOH using methyl red indicator which changes colour at pH 3.1-4.4 when, aluminium Al^{3+} ion remains practically neutral. The amount of HCl consumed may be obtained from the difference.



$$\therefore [\text{HCl}] \equiv [\text{NaHCO}_3] \equiv \frac{1}{2} [\text{MgCO}_3] \equiv \frac{1}{2} [\text{Mg}(\text{OH})_2] \equiv \frac{1}{3} [\text{Al}(\text{OH})_3].$$

\therefore 1000 ml of (N)HCl

$$\equiv 84 \text{ g. of NaHCO}_3 \equiv \frac{84.3}{2} \text{ g. of MgCO}_3 \equiv \frac{58}{2} \text{ g. of Mg}(\text{OH})_2 \equiv \frac{78}{3} \text{ g. of Al}(\text{OH})_3$$

Chemicals required :

1. Standard (N/20) oxalic acid solution.
2. (~ N/20) Sodium hydroxide solution.
3. (~ N/10) Hydrochloric acid solution.
4. Methyl orange indicator.
5. Phenolphthalein indicator.

Procedure :

1. Prepare 250 ml of standard (N/20) oxalic acid solution by accurate weighing.
2. Standardize the (~ N/20) sodium hydroxide solution by titrating the standard (N/20) oxalic acid solution with it using phenolphthalein indicator.
3. Standardize the (~ N/10) HCl solution (aliquot = 10 ml) by titrating it with the standard (~ N/20) NaOH solution using methyl orange indicator as usual. Colour change at the end point is from red to orange.
4. Weigh out accurately one/two tablets of the antacid sample in a 250 ml beaker, add 25 ml of water and a measured excess (~ (25/50/75 ml say $25 \times x$ ml) of the standard (~ N/10) HCl solution and warm gently till dissolution. Cool to room temperature and add 3 – 4 drops of methyl orange indicator. A red colour will indicate the presence of excess acid (HCl) and absence of any alkali. If the colour of the mixture at this stage is orange (i.e., not red), then add another measured volume (25/50/75 ml as required) of the standard (~ N/10) HCl solution to obtain a clear red solution.
5. Cool the solution to room temperature, transfer to a 100/250 ml volumetric flask and make up to the mark with distilled water. Take an aliquot of 25 ml from this prepared solution in a 250 ml of conical flask, add 1 – 2 drops of the methyl red indicator if necessary and then titrate the excess acid present with the standard and (N/20) NaOH solution till the colour of the solution changes from red to orange.
6. Calculate the alkali content of the antacid tablet in milli equivalent of NaOH per gram.

Calculation :

Let, (i) 250 ml of standard oxalic acid solution contains w_1 g. of $H_2C_2O_4 \cdot 2H_2O$.

\therefore Strength of standard oxalic acid = $(w_1/0.7879) (N/20)$

ii) If 25 ml of standard oxalic acid $\equiv V_1$ ml of NaOH solution.

\therefore Strength of NaOH solution

$$= \frac{25 \times w_1}{V_1 \times 0.7879} (N/20) = \left(\frac{25 \times w_1}{V_1 \times 0.7879 \times 20} \right) (N).$$

(iii) 25 ml of HCl solution

$$\equiv V_2 \text{ ml of } \frac{25 \times w_1}{V_1 \times 0.7879 \times 20} (N) \text{ NaOH}$$

$$\equiv \frac{25 \times w_1 \times V_2}{V_1 \times 0.7879 \times 20} \text{ ml of } (N) \text{ NaOH}$$

$\therefore (25 \times x) \text{ ml HCl}$

$$\equiv \frac{25 \times w_1 \times V_2 \times x}{V_1 \times 0.7879 \times 20} \text{ ml of } (N) \text{ NaOH.}$$

(iii) Let w_2 g. of the antacid tablet is dissolved in $(25 \times x) \text{ ml}$ of the HCl solution and diluted to 250 ml, of which 25 ml requires V_3 ml of the NaOH solution for neutralization, then,

$$\left(\frac{w_2}{10} \right) \text{ g. of the antacid tablet} + V_3 \text{ ml of } \frac{25 \times w_1}{V_1 \times 0.7879 \times 20} (N) \text{ NaOH.}$$

$$\equiv \left(\frac{25 \times x}{10} \right) \text{ ml of HCl}$$

$$\equiv \left(\frac{25 \times w_1 \times V_2 \times x}{V_1 \times 0.7879 \times 20 \times 10} \right) \text{ ml of } (N) \text{ NaOH}$$

$\therefore \left(\frac{w_2}{10} \right) \text{ g. of the antacid tablet}$

$$\equiv \left(\frac{25 \times w_1}{V_1 \times 0.7879 \times 20} \right) \left(\frac{V_2 \times x}{10} - V_3 \right) \text{ ml of } (N) \text{ NaOH.}$$

∴ w_2 g. of the antacid tablet

$$\equiv \left(\frac{25 \times w_1}{V_1 \times 0.7879 \times 20} \right) (V_2 \times x - 10V_3) \text{ ml of (N) NaOH.}$$

∴ 1 g. of the antacid tablet

$$\equiv \left[\left(\frac{25 \times w_1}{V_1 \times 0.7879 \times 20} \right) \left(\frac{V_2 \times x - 10V_3}{w_2} \right) \right] \text{ ml of (N) NaOH.}$$

∴ 1000 ml of (N) NaOH \equiv 40 g. NaOH \equiv 1 Eqv. of NaOH.

∴ 1 ml (N) NaOH \equiv m. eqv. of NaOH.

$$\therefore \left(\frac{25w_1}{V_1 \times 0.7879 \times 20} \right) \left(\frac{V_2 x - 10V_3}{w_2} \right) \text{ ml of (N) NaOH.}$$

$$\equiv \left(\frac{25 \times w_1}{V_1 \times 0.7879 \times 20} \right) \times \left(\frac{V_2 x - 10V_3}{w_2} \right) \text{ m. eqv. of NaOH}$$

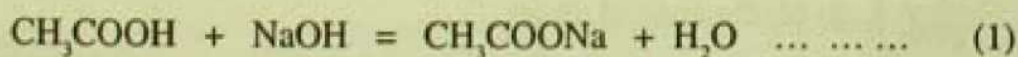
∴ Alkali content of antacid tablet

$$= \left(\frac{25}{0.7879 \times 20} \right) \left(\frac{w_1 (V_2 x - 10V_3)}{V_1 \times w_2} \right) \text{ m. eqv. / g..}$$

Experiment No. 15 : Estimation of acetic acid in commercial vinegar

Principle :

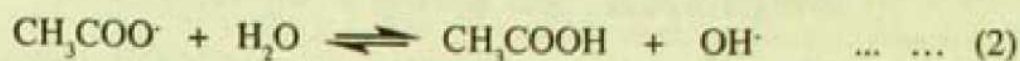
When acetic acid (CH_3COOH) is titrated with a strong base such as sodium hydroxide, sodium acetate (CH_3COONa) is produced :



$$\therefore [\text{NaOH}] \equiv [\text{CH}_3\text{COOH}]$$

i.e., 1000 ml of (N) NaOH \equiv 1000 ml of (N) acetic acid.

At the equivalence point, the solution will contain sodium acetate. Sodium ion (Na^+) is neutral. Acetate ion (CH_3COO^-), being the conjugate base of a weak acid, is a strong base and gives an alkaline reaction in water to produce unionised acetic acid molecule and equivalent amount of alkali (OH^-) is released :



\therefore at equilibrium, $[\text{CH}_3\text{COOH}] = [\text{OH}^-]$

pH of such a solution will be given by

$$\text{pH} = \frac{1}{2} \text{pK}_w + \frac{1}{2} \text{pK}_a + \frac{1}{2} \log c \quad \dots \dots \dots (3)$$

where, $\text{K}_w = [\text{H}^+] \times [\text{OH}^-] = \text{ionic product of water} = 10^{-14} \text{ at } 25^\circ\text{C},$

$\text{K}_a = \text{ionisation constant of acetic acid} (1.8 \times 10^{-5} \text{ at } 25^\circ\text{C})$

and $c = \text{molar concentration of acetate ion assuming no change of volume.}$

Thus, pH of (N/20) (i.e., 0.05 M) solution of sodium acetate will be equal to :

$$\text{pH} = \frac{1}{2}(14) + \frac{1}{2}(4.74) + \frac{1}{2} \log (0.05) = 8.72$$

So, phenolphthalein ($\text{pK}_{\text{in}} = 9.6$) will be a suitable indicator for this titration.

Chemicals required :

1. Standard (N/20) oxalic acid solution.
2. ~ (N/20) Sodium hydroxide solution.
3. Phenolphthalein indicator solution.
4. Sample vinegar solution.

Procedure :

1. Transfer 10 ml of the sample vinegar solution using a burette into a 250 ml volumetric flask, dilute to 250 ml and shake to mix uniformly.
2. Prepare 250 ml of standard (N/20) oxalic solution by accurate weighing.
3. Standardise the ~ (N/20) sodium hydroxide solution by titrating the standard (N/20) oxalic acid solution with it using phenolphthalein indicator (see Ch. – 2).
4. Take an aliquot of 25 ml of the prepared solution of the vinegar sample in a 250 ml conical flask, add 25 ml of distilled water, 2 – 3 drops of phenolphthalein indicator and titrate the mixture with the standard (N/20) sodium hydroxide up to a pink-red end point.

5. Calculate the amount of acetic acid in g/lit. of the vinegar sample.

Calculation :

Let, weight of oxalic acid in 250 ml solution = w g

\therefore Strength of oxalic acid solution = $(w/0.7879) (N/20)$

Let, 25 ml of standard oxalic acid $\equiv V_1$ ml of NaOH solution.

\therefore Strength of NaOH solution = $\left(\frac{25 \cdot w}{0.7879 \cdot V_1} \right) (N/20)$

Let, 25 ml of diluted solution of vinegar sample $\equiv V_2$ ml of standard NaOH solution.

\therefore Strength of dilute vinegar solution

$$= \frac{V_2 \times 25 \times w}{25 \times V_1 \times 0.7879} (N/20)$$

$$= \frac{V_2 \times w}{V_1 \times 0.7879} (N/20)$$

\therefore Strength of original solution of vinegar

$$= 10 \times \frac{V_2 \times w}{V_1 \times 0.7879} \times (N/20)$$

$$= \left(\frac{V_2 \times w}{V_1 \times 0.7879 \times 2} \right) (N)$$

Since the formula weight of acetic acid (CH_3COOH) is 60 = its equivalent weight

\therefore strength of acetic acid in g. / lit.

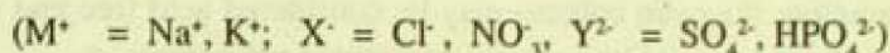
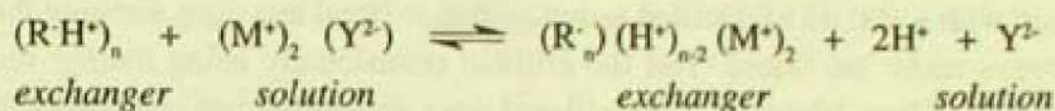
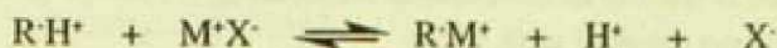
$$= \left(\frac{60}{0.7879 \times 2} \right) \cdot \left(\frac{w V_2}{V_1} \right) \text{ g./lit}$$

$$= 38.076 \left(\frac{w V_2}{V_1} \right) \text{ g./lit}$$

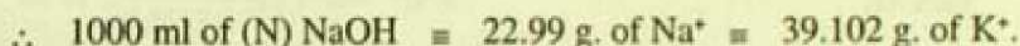
Experiment No. 16 : Determination of Na^+ / K^+ in a given solution by ion-exchange method.

Principle :

When known volume of a solution containing Na^+ or K^+ ion in the form of their salts with strong acids, e.g., HCl , HNO_3 , H_2SO_4 is passed through a column of cation exchange resin in H^+ -form, an equivalent amount of H^+ ion is released and the metal ion (Na^+ or K^+) is held by the resin :



The liberated acid in the effluent may be estimated by titrating with a standard solution of NaOH .



Chemicals and Apparatus required :

i) Standard (N/50) oxalic acid solution :

To be prepared by accurate weighing (0.3152 g./250 ml solution)

ii) (~ N/50) NaOH solution : ~ 0.3 – 0.5 g. of (A.R.) NaOH / 250 ml

iii) Strongly acidic cation exchange resin : Dowex – 50, or, Amberlite IR – 120, or, Zeolit – 225 (50 – 100 or 15 – 50 mesh).

iv) Methyl red indicator : 0.1 – 0.2 % solution in 60% ethanol.

v) 2(M) HCl (A.R.) solution : (1 : 6) HCl

vi) (A.R.) NaCl / KCl or NaNO_3 / KNO_3 : ~ 0.2 – 0.4 g. of the salt / 100 ml of solution in distilled water.

Procedure :

i) Plug the ion-exchange column (15 cm \times 1 cm) at its bottom with glass wool and attach a rubber tubing with a pinch cook for adjusting the rate of flow. Alternatively use a U-type ion-exchange column and plug the bottom with glass wool. (See Ch. 8).

- ii) Place ~ 10 – 15 g. of the dry resin in a beaker and add 50 ml of 2(M) HCl and stir thoroughly, allow to stand for ~ 30 minutes. By this time the swelling of the resin will be complete and it will be converted to its H^+ -form.
- iii) Partly fill the ion-exchange column with distilled water. Remove any air bubble that may adhere to the glass wool plug or to the wall of the tube.
- iv) Insert the resin in to the column by washing with water, and draining out the water inside the tube as required. Adjust the height of the resin in such a way that there remains sufficient space at the top of the column for holding ~ 15 – 20 ml of liquid. Keep the resin head always covered with water.
- v) Wash the resin with ~ 100 ml of distilled water, adding ~ 10 ml at a time, keeping the resin top always under the liquid. Test the effluent occasionally using methyl red indicator solution. When 10 drops of the effluent does not impart any red colour to the indicator solution, the resin column may be considered acid free and ready for exchange. Close the stopper. (Alternatively, test with a pH paper).
- vi) Place a 250 ml conical flask under the column for collecting the effluent. Place 10 ml of the test solution which is ~ (M/50) in Na^+ or K^+ on the top of the column using a pipette. Release the stopper and adjust the rate of flow ~ 15 – 20 drops per minute.
- vii) When the level of the experimental solution just approaches the resin top, start washing the column with distilled water, adding ~ 10 ml at a time, always keeping the resin covered with water. Test the effluent with methyl red indicator solution after 5 – 6 washings. If a red colour is imparted, add the red solution quantitatively into the main bulk of the effluent. Continue the process of washing with water and testing with methyl red indicator solution till 10 drops of the effluent do not impart red colour to the methyl red solution. Close the stopper.
- viii) Titrate the combined effluent and the washings with standard (~ M/50) NaOH solution using methyl red indicator, till the red colour of the solution changes to yellow. Record the titre (V).
- ix) Standardization of NaOH solution.

Take an aliquot of 10 ml of the standard (N/50) oxalic acid solution in 250 ml conical flask, dilute to ~ 100 ml with distilled water, add 2 – 3 drops of phenolphthalein indicator and titrate with (~ N/50) NaOH solution till the colour changes to red. Record the titre (V' ml).
- x) After the experiment is over, pass 100 ml of 2(M) HCl through the column to regenerate the H^+ -form of the resin for future use. Wash with distilled water as before to remove

any free acid from the column and close the stopper. The resin top should always be kept under water.

- xi) Calculate the total quantity of Na^+/K^+ in the sample.

Calculation :

Strength of oxalic acid solution = $(w/0.3152) (M/50)$

where, w = wt. of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in 250 ml solution.

\therefore 10 ml of standard oxalic acid

$$\equiv V' \text{ ml of NaOH solution}$$

\therefore Strength of NaOH solution

$$= \left(\frac{10 \times w}{0.3152 \times V'} \right) (N/50)$$

\therefore 10 ml of sample solution

$$\equiv V \text{ ml of } \left(\frac{10 \cdot w}{0.3152 \times V'} \right) (N/50) \text{ NaOH}$$

$$\equiv \left(\frac{10 \cdot w \cdot V}{0.3152 \times V' \times 50} \right) \text{ ml of } (N) \text{ NaOH}$$

\therefore 100 ml of sample solution

$$\equiv \left(\frac{100 \cdot w \cdot V}{0.3152 \times V' \times 50} \right) \text{ ml of } (N) \text{ NaOH}$$

$$\equiv \left(\frac{100}{0.3152 \times 50} \right) \times \left(\frac{wV}{V'} \right) \text{ ml of } (N) \text{ NaOH}$$

$$\equiv \left(\frac{22.99 \times 100}{1000 \times 0.3152 \times 50} \right) \times \left(\frac{wV}{V'} \right) \text{ g. of Na}$$

$$= 0.1459 \times (wV/V') \text{ g. of Na}$$

$$\equiv \left(\frac{39.102 \times 100}{1000 \times 0.3152 \times 50} \right) \times (wV/V') \text{ g. of K}$$

$$\equiv 0.2481 \times (wV/V') \text{ g. of K.}$$

Chemicals required :

- i) Standard (M/50) Zn-acetate solution.
Strength = $(w/1.0969)$ (M/50), where, w = wt. of Zn-acetate dihydrate per 250 ml of 2% NH_4Cl (A.R.) solution.
- ii) (~ M/50) EDTA solution : ~ 1.8-2.0 g. of $\text{Na}_2\text{H}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ / 250 ml.
- iii) NH_4Cl - NH_3 -Buffer solution ($\text{pH} = 10$) : Dissolve 7 g. of (A.R.) NH_4Cl in ~ 57 ml of conc. NH_3 and dilute to 100 ml.
- iv) Mg-EDTA complexe : Dissolve 0.472 g. of $\text{Na}_2\text{H}_2\text{EDTA}$ + 0.312 g. of (A.R.) $\text{Mg} \cdot \text{SO}_4 \cdot 7\text{H}_2\text{O}$ in 50 ml of distilled water and dilute to 100 ml.
- v) EBT – indicator : 0.05 g. of EBT in 5 g. of KCl or NaCl
- vi) Sample : Natural chalk or black board chalk (~ 0.2-0.3) g / 100 ml.

Procedure :

- i) Dissolution of chalk :

Weigh out accurately 0.2-0.3 g. of the finely powdered chalk sample in a 250 ml beaker. Add 10 ml of distilled water and 5 ml of (A.R.) conc. HCl. Warm the mixture gently on a low flame on an asbestos board or on a hot plate till dissolution. Digest and evaporate gently (use a fume hood) to almost dryness. Bake for 4-5 minutes, cool to room temperature and take up with 50 ml of dilute (1:6) HCl. Transfer quantitatively into a 100 ml volumetric flask and make the volume up to the mark with distilled water and mix uniformly.

- ii) Standardisation of EDTA solution :

Pipette out 25 ml of standard (M/50) Zn-acetate solution in 250 ml conical flask, add 20 ml of water and 5 ml of NH_4Cl - NH_3 buffer solution ($\text{pH} = 10$) and a pinch of EBT indicator powder. Titrate with EDTA solution till the colour of the solution changes from wine red to blue. Record the titre (V_1 ml).

- iii) Estimation of calcium in chalk :

Take an aliquot of 25 ml of the sample chalk solution in a 250 conical flask, neutralize with drops of (1 : 1) aqueous ammonia till the smell of ammonia is perceived. Add 2-3 drops of MgEDTA solution, 5 ml of NH_4Cl - NH_3 buffer solution ($\text{pH} = 10$) and a pinch of EBT indicator. The solution assumes a wine red colour. Titrate with standard (M/50) EDTA solution till the colour changes to blue. Record the titre (V_2 ml).

- iv) Calculate the % of CaCO_3 / CaSO_4 in the sample.

Calculation :

Strength of standard Zn-acetate solution = $(w/1.0969) (M/50)$

25 ml of standard Zn-acetate $\equiv V_1$ ml of EDTA.

$$\therefore \text{Strength of EDTA} = \left(\frac{25 \times w}{1.0969 \times V_1} \right) (M/50)$$

Ca^{2+} in 25 ml sample solution $\equiv V_2$ ml of $\left(\frac{25 \times w}{1.0969 \times V_1} \right) (M/50)$ EDTA

$$\equiv \left[\left(\frac{25}{1.0969 \times 50} \right) \times \frac{wV_2}{V_1} \right] \text{ ml of (M) EDTA}$$

\therefore Total Ca^{2+} in 100 ml of

$$\equiv \left(\frac{100 \times 25}{25 \times 1.0969 \times 50} \right) \times \frac{wV_2}{V_1} \text{ ml of (M) EDTA}$$

$$\equiv 1.8233 \times \left(\frac{wV_2}{V_1} \right) \text{ ml (M) EDTA}$$

$$= 0.04008 \times 1.8233 \times (wV_2/V_1) \text{ g. of Ca}$$

$$= 0.07308 \times (wV_2/V_1) \text{ g. of Ca}$$

$$\equiv 0.10008 \times 1.8233 (wV_2/V_1) \text{ g. of CaCO}_3$$

$$= 0.18248 \times (wV_2/V_1) \text{ g. of CaCO}_3$$

$$\equiv 0.13614 \times 1.8233 \times (wV_2/V_1) \text{ g. of CaSO}_4$$

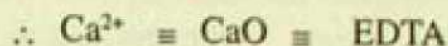
$$= 0.24823 \times (wV_2/V_1) \text{ g. of CaSO}_4$$

Experiment No. 18 : Estimation of calcium in milk powder

Principle :

When dry milk powder is heated to redness, the organic matters decompose and volatilise. The ash that is produced contains K_2O , CaO , P_2O_5 , Na_2O , Cl^- and SO_4^{2-} as major constituents and MgO and Fe_2O_3 as minor/trace constituents depending upon the source. By

extracting the ash with dilute nitric acid, the metallic constituents are brought into solution mainly as their nitrate salts together with some phosphate, sulfate and small amount of chloride. Complexometric EDTA titration of this extract in $\text{NH}_4\text{Cl-NH}_3$ buffer medium gives the total quantity of the metals, which may be conveniently expressed in terms of CaO, as EDTA forms 1:1 complexes with all these metal ions under this condition,



$$\therefore 1000 \text{ ml of (M) EDTA} \equiv 40.08 \text{ g. of Ca} \equiv 56.07 \text{ g. of CaO.}$$

Since phosphate is present, which may precipitate the metal ions in ammoniacal medium, a back titration procedure, by treating the sample solution with a measured excess of standard EDTA in $\text{NH}_4\text{Cl-NH}_3$ buffer (pH = 10) medium and then titrating the excess EDTA with a standard Zn-acetate solution gives better result than the direct titration of the sample solution with EDTA at this condition.

Note : i) Iron can be rendered harmless by adding a small amount of sodium sulphide.

ii) Estimation of Ca by direct titration with EDTA at high pH (~ 12) using murexide, calcon, or, Patton Reeder's indicator may not be convenient due to the presence of phosphate which may precipitate some calcium as phosphate.

Chemicals and Apparatus required :

- 1) Standard (M/50) Zn-acetate : To be prepared by accurate weighing : [$\sim 1 \text{ g}$ of (A.R.) $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$. (w. g. say in 250 ml of 2% NH_4Cl solution. Strength = (w/1.0969) (M/50)].
- 2) ($\sim \text{M/50}$) $\text{Na}_2\text{H}_2\text{EDTA}$ solution.
- 3) HNO_3 (A.R.)
- 4) $\text{NH}_4\text{Cl-NH}_3$ buffer (pH = 10) solution.
- 5) Eriochrom Black – T indicator powder/solution.
- 6) Silica Crucible/Porcelain Crucible with lid.
- 7) Tongs
- 8) Clay pipe triangle/silica pipe triangle
- 9) Desiccator with silica gel drier.

Procedure :

(i) Extraction of Ca^{2+} from milk powder :

Dry the sample of milk powder (if necessary) by placing in a desiccator. Weigh out accurately $\sim 1\text{-}2\text{ g}$ (say $w\text{ g.}$) of the dry milk powder into a silica/porcelain crucible. Place the lid and decompose the sample by gentle heating by placing the crucible on a clay/silica pipe triangle, then heat below redness for about an hour. Cool to room temperature, moisten the contents with a few drops of conc. HNO_3 and heat as before for ~ 30 minutes. Cool to room temperature and extract with minimum volume of (1:5) dilute HNO_3 . Filter through Whatman No. 1 filter paper, wash with water and collect the filtrate and the washing into a 250 ml volumetric flask and make the volume up to the mark with distilled water. Discard the residue if any and preserve the filtrate (sample solution) for estimation of Ca.

(ii) Standardisation of EDTA solution :

Pipette out 25 ml of the ($\sim \text{M}/50$) EDTA solution into a 250 ml conical flask, dilute with 20 ml of distilled water, add 5 ml of $\text{NH}_4\text{Cl-NH}_3$ buffer ($\text{pH} = 10$) solution a pinch of EBT indicator powder, or 3-4 drops of the indicator solution, and titrate with standard ($\text{M}/50$) Zn-acetate solution till the colour changes from blue to wine red. Record the titre (V_1 ml).

(iii) Estimation of Ca^{2+} :

Take an aliquot of 100 ml of the sample solution in a 500 ml conical flask, add a measured excess [25/50/75 ml say $(25 \times x)$ ml] of standard ($\text{M}/50$) EDTA solution. Neutralize with (1:1) ammonia solution till the smell of ammonia is perceived. Add 10 ml of the $\text{NH}_4\text{Cl-NH}_3$ buffer ($\text{pH} = 10$) solution and a pinch (or 3-4 drops) of the EBT indicator, titrate the excess EDTA with standard ($\text{M}/50$) zinc-acetate solution till the colour changes from blue to wine red. Record the titre (V_2 ml).

(iv) Calculate the % of CaO in the sample of milk powder :

Calculation :

Strength of Zn-acetate = $(w/1.0969)$ ($\text{M}/50$)

where, w = wt. of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ per 250 ml.

25 ml of EDTA $\equiv V_1$ ml of $(w/1.0969)$ ($\text{M}/50$) Zn-acetate

$\therefore (25 \times x)$ ml of EDTA $\equiv (V_1 \times x)$ ml of $(w/1.0969)$ Zn-acetate

$(25 \times x)$ ml of EDTA $\equiv \text{Ca in 100 ml of sample solution} + V_2 \text{ ml of } (w/1.0969) (\text{M}/50) \text{ Zn-acetate}$

∴ Ca in 100 ml of sample solution

$$\begin{aligned}
 &= (V_1x - V_2) \text{ ml of } (w/1.0969) \text{ (M/50) Zn-acetate} \\
 &= (V_1x - V_2) \times [w / (1.0969 \times 50)] \text{ ml of (M) Zn-acetate} \\
 &= (V_1x - V_2) \times [w / (1.0969 \times 50)] \text{ ml of (M) Ca} \\
 &= 0.04008 \times (V_1x - V_2) \times [w / (1.0969 \times 50)] \text{ g. of Ca} \\
 &= 0.05607 \times (V_1x - V_2) \times [w / (1.0969 \times 50)] \text{ g. of CaO}
 \end{aligned}$$

∴ Total Ca in 250 ml sample solution containing w' g. of Milk powder

$$\begin{aligned}
 &= 0.04008 \times 2.5 \times (V_1x - V_2) \times [w / (1.0969 \times 50)] \text{ g.} \\
 &= 1.8269 \times 10^{-3} \times [w (V_1x - V_2) \text{ g.}]
 \end{aligned}$$

∴ Total CaO in 250 ml of sample solution containing w' g of milk powder

$$\begin{aligned}
 &= 0.05607 \times 2.5 \times (V_1x - V_2) \times [w / (1.0969 \times 50)] \\
 &= 2.5558 \times 10^{-3} \times w(V_1x - V_2) \text{ g.}
 \end{aligned}$$

$$\therefore \% \text{ of Ca} = 0.18269 \times [w(V_1x - V_2) / w'] \%$$

$$\% \text{ of Ca O} = 0.25558 \times [w(V_1x - V_2) / w'] \%$$

Chapter - 12

Colourimetric Estimations

Experiment – 1 : Colourimetric Estimation of Mn in (i) Commercial H_3PO_4 (ii) sample solution.

Principle :

Commercial H_3PO_4 may contain small amount of Mn originating from phosphate minerals. Low Mn content can be conveniently estimated by colourimetric method. The colourimetric determination is based on *Lambert-Beer's law*, according to which the molar absorbance (A) of a light absorbing substance is given by

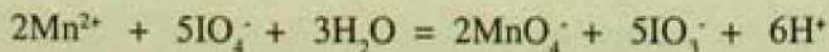
$$A = \epsilon cl$$

where, l is the path length (usually 1 cm), c is the concentration in molarity and ϵ is the molar extinction coefficient. If the absorbance (A) of a series of solutions of known concentrations of the substance to be determined is plotted against concentration (c), a straight line passing through origin is obtained. The molar extinction coefficient, ϵ , may be obtained from the slope of this straight line. Such a curve is called a *calibration curve*. The range of concentration of the substance, where the absorbance vs. concentration curve is linear, is the useful range of concentration for colourimetric determination.

Unknown concentration of the substance in a sample solution may be determined by measuring its absorbance for the light of same wave length and then extrapolating the calibration curve or by simply dividing the experimental absorbance by the extinction coefficient.

In colourimetric determinations, optical filters are often used for isolating the desired spectral region from the undesired ones. Light-filters in the wavelength region 500-560 nm are generally used in the determination Mn as MnO_4^- . Alternatively, a spectrophotometer may be used and measurement may be made at 520 nm.

Periodate ion (IO_4^-) quantitatively oxidises Mn^{2+} to permanganic acid (HMnO_4) in hot dilute nitric or sulphuric acid medium :



The resulting MnO_4^- is determined colourimetrically / spectrophotometrically.

$$\therefore [\text{MnO}_4^-] = [\text{Mn}]$$

Chemicals and Apparatus required :

- (~ N/20) KMnO_4 solution : Dissolve 0.4 ~ 0.5 g. of KMnO_4 in distilled water and dilute to 250 ml.
- (A.R.) KIO_4
- (i) Commercial H_3PO_4 , or, sample containing manganese (ii) $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (F.W. = 169.05) or, $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ (F.W. = 223.05), (A.R.), ~ $10^{-2}(\text{M})$ solution in 2 (N) H_2SO_4 .
- Standard (N/20) oxalic acid or sodium oxalate solution : To be prepared by accurate weighing
- Colourimeter/Spectrophotometer with matched cells.

Procedure :

1. *Standardisation of KMnO_4 solution :*

To be standardized against standard oxalic acid or sodium oxalate solution (see Ch-4, Permanganometry). Dilute 10 ml of this solution to 50 ml in a 50 volumetric flask to obtain a standard (N/100) KMnO_4 solution i.e., (M/500) KMnO_4 solution.

2. *Preparation of standard MnO_4^- solutions :*

Take 0.5, 1.0, 2.0, 4.0, 6.0, 8.0 and 10.0 ml of the standard ~ (N/100) KMnO_4 solution in separate 50 ml volumetric flasks and dilute each solution upto the mark with distilled water and calculate their concentrations in ppm of Mn.

3. *Preparation of the test solution :*

Transfer the total quantity of the sample solution containing less than 20 ppm of Mn into a 250 ml beaker, add 25 ml of 2(N) H_2SO_4 , 5 ml of Mn-free (A.R.) H_3PO_4 and 0.5-0.6 g. of (A. R.) KIO_4 . Heat the mixture to ~ 90°C and keep the solution hot for ~10 minutes. Allow to cool, transfer the solution quantitatively in to a 100 ml volumetric flask and dilute upto the mark with distilled water.

4. *Measurement of absorbance :*

Set the colourimeter to 100% transmittance using the light filter of wavelength 545 nm for a blank solution containing a mixture of 1 ml (A.R.) syrupy H_3PO_4 and 20 ml of 2(N) H_2SO_4 . Measure the absorbance of the standard KMnO_4 solutions as well as that of the test solution against this blank solution and record the data in a tabular form.

5. *Calibration curve :*

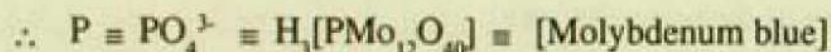
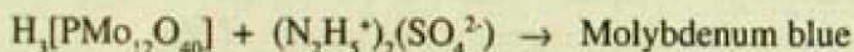
Plot the absorbance of the standard permanganate solutions against their concentrations in ppm of Mn and draw the best straight line passing through the origin. Determine the concentration (ppm) of Mn in the sample solution from the calibration curve by graphical extrapolation as usual.

- Notes :** (i) In colourimetric determination of Mn the solution should not contain more than 2 mg of manganese per 100 ml, otherwise the colour will be too dark to match easily.
- (ii) ~ 1.1 g of potassium periodate is required to oxidise each 0.1 g of Mn^{II} .

Experiment No. 2 : Colourimetric estimation of phosphate as molybdenum blue complex.

Principle :

Orthophosphate (PO_4^{3-}) and molybdate (MoO_4^{2-}) condense in acid medium to give the heteropolyacid, molybdophosphoric acid, or, phosphomolydic acid, $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$, which upon selective reduction (eg. with hydrazine sulfate, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$) produces blue colour due to molybdenum blue of uncertain composition. The resulting blue colour exhibits λ_{max} at 820-830 nm. The intensity of the blue colour is, however, proportional to the quantity of phosphate initially incorporated in the heteropoly acid. If acidity of the medium at the time of reduction is ≥ 0.5 (M) in H_2SO_4 , then hydrazinium sulfate ($(\text{N}_2\text{H}_5^+)_2(\text{SO}_4^{2-})$) is the actual reductant.



$$\equiv [\text{Intensity of blue colour}] \equiv \text{Absorbance (A)}$$

This absorbance intensity (A) of the blue colour obeys Beer's Law if the solution contains (0.5 – 4.0) ppm of phosphorus in the form of phosphate. Applying Lambert Beer's Law to the molybdenum blue colour,

$$A = \epsilon \cdot [\text{Phosphate}] \cdot l$$

where, ϵ = extinction coefficient of molybdenum blue, l = optical path length of the solution. Phosphate concentration in an unknown (uk) solution, $[\text{phosphate}]_{\text{uk}}$ may be determined by comparing the absorbance intensity (A)_{uk} due to molybdenum blue colour obtained for the unknown solution with the absorbance intensity (A)_k obtained for a phosphate solution of known concentration, $[\text{phosphate}]_k$ using the relation :

$$\frac{(A)_{\text{uk}}}{(A)_k} = \frac{[\text{phosphate}]_{\text{uk}}}{[\text{phosphate}]_k}$$

or, by graphically comparing the absorbance of the unknown solution with those of a series of solutions of known concentration following Beer's Law, using a calibration curve.

Reagents and apparatus :

- 1) 2.5% $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (A.R.) in 9(N) H_2SO_4 , (A) (250 ml).
- 2) 0.15% (A.R.) Hydrazine sulfate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$) in water (B) (100 ml).
- 3) $(1-2) \times 10^{-3}$ (M) KH_2PO_4 in water : 0.2197 g. of (A.R.) KH_2PO_4 (F.W. = 136.13) per litre of the solution. (1 ml \equiv 0.05 mg of P.)

$$\therefore \text{Strength} = \frac{0.2197}{136.13} \text{ (M)} = 1.61 \times 10^{-3} \text{ (M)}$$

- 4) (1 : 4) H_2SO_4 (A.R.) i.e., 9(N) H_2SO_4 .
- 5) Spectrocolourimeter with a pair of matched cells.
- 6) Volumetric flasks : 50 ml (5 – 6) pes., 100 ml (1 pc.), 250 ml (1 pc.), 1000 ml (1 pc.).
- 7) Graduated pipettes : 2 ml, 5 ml, 10 ml.
- 8) Hot water bath.

Procedure :

- (i) Just before required, mix 25 ml of the molybdate solution (A) and 10 ml of the hydrazine sulfate solution (B) and dilute to 100 ml. Final acidity of this "Reagent Solution" will be 2.25 (N) in H_2SO_4 .
- (ii) Determination of λ_{max} / best filter of molybdenum blue solution :
Take an aliquot of appropriate volume (1-4 ml) of the 1.61×10^{-3} (M) phosphate solution in a 100 ml beaker, add 20 ml of the "reagent solution" and dilute with 10 ml of distilled water. Stand for ~ 10 minute on a boiling water bath. Cool to room temperature, transfer qualitatively into a 50 ml volumetric flask and make up to the mark with distilled water. Measure the absorbance of the solution against water as blank using a spectrophotometer / colourimeter at different wave lengths (900-400 nm) or using different filters and find the λ_{max} (best filter). The volume of the aliquot of phosphate solution is to be so adjusted that the absorbance values at the λ_{max} after dilution falls within the range, 0.1 – 0.7, beyond which the sensitivity of the instrument will be very low.
- (iii) Verification of Beer's Law & determination of useful range of concentration : Prepare the following series of solutions each of total volume 50 ml with an acidity of ~1(N) in H_2SO_4 by mixing different known volumes (0.5-4 ml) of the phosphate solution with sufficient excess (20 ml) of the reagent solution. Dilute each solution with 10 ml of distilled water and heat each solution for 10 minutes on a hot water bath. Cool to room temperature, transfer quantitatively into 50 ml volumetric flasks and make up to the marks with distilled water. Measure the absorbance of all the solutions using water as blank at the λ_{max} / best filter determined earlier.

Set	1	2	3	4	5	6	Unknown
Vol. $1.6 \times 10^{-3}(\text{M})$ $\text{KH}_2\text{PO}_4(\text{ml})$	0.5	1.0	2.0	2.5	3.0	4.0	(1-4)
Vol. Reagent (ml)	20	20	20	20	20	20	20
Total vol. (ml)	50	50	50	50	50	50	50
$[\text{PO}_4^{3-}](\text{M}) \times 10^5$	1.61	3.22	6.44	8.05	9.66	12.88	—
P (ppm)	0.50	1.00	2.00	2.50	3.00	4.00	—
Absorbance (A) (path length = 1 cm)	—	—	—	—	—	—	—

(iv) Calibration curve.

Plot the absorbance of the solutions (set 1-6) against the concentration of phosphate in units of $10^{-5}(\text{M})$ or in (ppm) of phosphorus and draw the best straight line passing through the origin and the experimental points. The range of concentration in which the plot is linear is the useful range where, Beer's Law is obeyed and is suitable for colourimetric determination of phosphate.

(v) Determination of phosphate in unknown solution :

Take a specified volume of the unknown phosphate solution (its concentration has to be within the useful range of concentration), treat it according to procedure (iii) described before and measure its absorbance. Find the concentration of phosphate solution or the amount of P (ppm) from the calibration curve (iv).

Note : If the colour intensity (A_{uk}) of the unknown phosphate solution is too intense or too light, as such, the phosphate concentration does not fall within the useful range of concentration in which Beer's Law is obeyed, use the appropriately diluted or concentrated solution as required.

(vi) Calculation :

$$1000 \text{ ml of (M) phosphate} \equiv \text{PO}_4^{3-} \equiv \text{P} \equiv 30.9738 \text{ g. of P} \\ \equiv 30973.8 \text{ mg of P}$$

$$\therefore 1(\text{M}) \text{ phosphate} \equiv 30973.8 \text{ ppm of P}$$

$$(\because \text{ppm} = \text{mg} / 1000 \text{ ml})$$

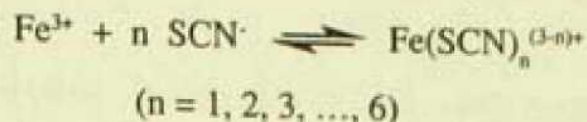
$$\therefore \text{ppm of P} = (\text{strength of phosphate solution in moles/lit}) \times 30973.8.$$

Molar strength of phosphate solution may be obtained from the calibration curve.

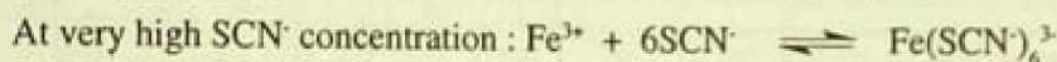
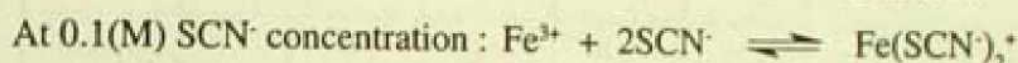
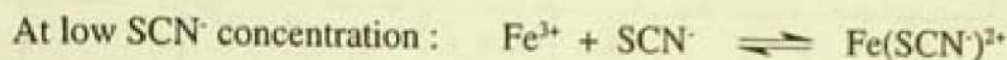
Experiment No. 3 : Colourimetric estimation of Fe^{III} as $\text{Fe}^{\text{III}}(\text{SCN})^{2+}$ complex

Principle :

In dilute 0.05 – 0.5 (M) acid medium. Fe^{3+} reacts with thiocyanate (SCN^-) ion to produce the red coloured Fe^{III} -thiocyanate complexes according to



The composition of the complex prevailing in solution of course depends upon thiocyanate concentration :



The red coloured Fe^{III} - SCN^- mixture at $[\text{SCN}^-] = 0.3$ (M) shows λ_{max} at 500 nm with $\epsilon = 7900 \text{ mol}^{-1} \cdot \text{cm}^2$.

For colourimetric estimation of Fe^{III} as Fe^{III} - SCN^- complex the following conditions are to maintained :

- (i) Large excess of SCN^- is to be used since this increase the stability of the complex and intensity of colour.
- (ii) Acidity (0.05 – 0.5) (M) is to be maintained with respect to HNO_3 or HCl to prevent hydrolysis of Fe^{3+} (aq) ion according to



H_2SO_4 is not recommended, since SO_4^{2-} may form complex with Fe^{3+} .

Chemicals and equipment :

- (i) Standard (M/100) Zn acetate solution, (~ M/100) EDTA solution, NH_4Cl - NH_3 buffer (pH = 10) solution.
- (ii) 15% K SCN or NH_4SCN solution in water.
- (iii) 2×10^{-3} (M) Fe^{III} solution : Dissolve ~ 1.0 g of (A.R.) Fe^{III} -alum in 10 ml of (A.R.) HCl and dilute to 1000 ml. The resulting solution will be ~ 0.12 (M) in HCl . The extract strength of this Fe^{III} -solution is to be checked by titrating 50 ml of this solution against standard (M/100) EDTA solution at pH = 2 using 3-4 drops of 15% KSCN or NH_4SCN solution. Colour change at the end point will be from red to colourless (see Ch-6).

- (iv) 2(M) HCl (A.R.).
- (v) Colourimeter / Spectrophotometer with a pair matched cells.
- (vi) Volumetric flasks – 50 ml : (5-6) pcs.
- (vii) Graduated pipettes : 2 ml, 5 ml, 10 ml.

Procedure :

- (i) Prepare the following series of solutions each of total volume = 50 by mixing different volumes of 2×10^{-3} (M) Fe^{III} solution with large excess of thiocyanate solution maintaining the acidity ~ 0.5 (M) in HCl.

Set	1	2	3	4	5	6	7
Vol. of 2×10^{-3} (M) Fe^{III} (ml)	0.5	1.0	2.0	3.0	4.0	5.0	Unknown
Vol. of 15% KSCN (ml)	10	10	10	10	10	10	10
Vol of 2(M) HCl (ml)	12.5	12.5	12.5	12.5	12.5	12.5	12.5
$[\text{Fe}^{\text{III}}](\text{M}) \times 10^5$	2	4	8	12	16	20	—
Fe^{III} (ppm)	2.24	4.48	8.96	13.44	17.92	22.4	—
Absorbance (A) path length = 1 cm	—	—	—	—	—	—	—

- (ii) Take any one of these solutions (1-6) and determine its absorbance at different wave length (700 – 400) nm hence find the λ_{max} , or find the best filter as usual.
- (iii) Measure the absorbance of the remaining solutions only at the λ_{max} , or, with the best filter, use suitable volumes of the Fe^{III} solution so that the absorbance readings are within 0.1 to 0.7.
- (iv) Calibration curve : Plot the absorbance against concentration of Fe^{III} in units of 10^{-5} (M) or in ppm and draw the best straight line through the origin and the experimental points, hence find the useful range of concentration where Beer's Law ($A = \epsilon . c . l$) is obeyed (where, c = concentration in moles/lit and l = fixed optical path length in cm.).
- (v) Treat the unknown Fe^{III} solution with the 15% K SCN and 2(M) HCl solution in the same manner and measure its absorbance at the λ_{max} / best filter hence find its concentration from the calibration curve.

(vi) **Calculation :**

1000 ml (M) Fe^{III} solution \equiv 55847 mg. of Fe.

\therefore 1(M) Fe solution \equiv 55847 ppm of Fe.

(\because ppm = mg / 1000 ml)

\therefore 2×10^{-3} (M) Fe^{III} solution \equiv 111.7 ppm of Fe.

If v ml of 2×10^{-3} (M) Fe^{III} is diluted to 50 ml, then, concentration of Fe^{III} in the diluted solution will be :

$$= v.f. 4 \times 10^{-5} \text{ (M) } \text{Fe}^{\text{III}} \equiv 2.23 \times v \times f \text{ (ppm) of Fe.}$$

where, f = factor of 2×10^{-3} (M) Fe^{III} solution, to be determined by EDTA titration. EDTA solution has to be standardised against standard Zn-acetate solution in $\text{NH}_4\text{Cl-NH}_3$ buffer solution (pH = 10) using EBT indicator as usual. (See Chap.6)

Experiment No. 4 : Colorimetric estimation of Fe^{II} + Fe^{III} mixture

Principle :

Fe^{2+} ion reacts with 1, 10 phenanthroline (phen) in weakly acidic medium (pH : 2-5 in HCl or HNO_3 but not H_2SO_4) to form the intensity red coloured "*ferroin*" complex, $\text{Fe}(\text{phen})_3^{2+}$, which shows λ_{max} in the region 480 – 520 nm [precisely in λ_{max} and ϵ values are: 490 nm (10,590) and 505 nm (11,080)].



Beer's Law is obeyed in the range of concentration less than 6 ppm of Fe^{2+} . If Fe^{3+} ion is also present in the solution, it has to be reduced to Fe^{2+} ($\text{Fe}^{3+} + e \rightarrow \text{Fe}^{2+}$) using a suitable reducing agent, viz., hydroquinone or hydroxyl amine hydrochloride. Colourimetric estimation of the ferroin complex after reduction of Fe^{3+} to Fe^{2+} will give the total amount of Fe equal to $\text{Fe}^{\text{II}} + \text{Fe}^{\text{III}}$ and such estimation without reduction gives Fe^{II} only. Fe^{III} may be obtained from the difference.

Chemicals and equipment :

- (i) 0.001 (M) Fe^{II} solution : Dissolve \sim 0.2 g (precisely 0.196 g) of A.R. Mohr's salt, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ in 0.01 (M) HNO_3 solution in a 100 ml volumetric flask and make up to the mark with the same acid. This gives a \sim 0.005(M) Fe^{II} solution.

Accurately dilute 20 ml of this solution with 0.01(M) HNO_3 to 100 ml in a volumetric flask (100 ml) to obtain a ~ 0.001 (M) Fe^{II} solution.

- (ii) 0.001 (M) Fe^{III} solution : Dissolve ~ 0.25 (precisely 0.241 g) of Fe^{III} -alum, $(\text{NH}_4)_2\text{SO}_4\cdot\text{Fe}_2(\text{SO}_4)_3\cdot 24\text{H}_2\text{O}$ in 0.01 (M) HNO_3 in a 100 ml volumetric flask and make up to the mark with the same acid. This gives a ~ 0.005 (M) Fe^{III} solution. To obtain a 0.001(M) Fe^{III} solution, accurately dilute 20 ml of this solution with 0.01(M) HNO_3 to 100 ml in a 100 ml volumetric flask.
- (iii) Hydroquinone : 1% solution in acetic acid / acetate buffer (pH = 4.5), [65 ml of 0.1(M) acetic acid (1 : 170) and 35 ml of 0.1(M) sodium acetate (1%)], to be stored in a refrigerator.
- (iv) 1,10 phenanthroline solution : 0.5% solution in 0.01 (M) HNO_3 .
- (v) Sodium acetate : 25% aqueous solution (~ 2 (M)).
- (vi) Bromophenol blue indicator : 0.1% solution in 20% alcohol.

- Note:** (i) Exact strength of Fe^{II} solution may determined by titrating 10 ml of the 0.005 (M) Fe^{II} solution with a standard (N/100) $\text{K}_2\text{Cr}_2\text{O}_7$ in 2(N) H_2SO_4 medium using BDS indicator in presence of H_3PO_4 or NH_4HF_2 as usual (see Ch-5).
- (ii) Exact strength of Fe^{III} solution may be determined by titrating 10 ml of the 0.005(M) Fe^{III} solution with standard (M/100) EDTA solution at pH \sim 2, using NH_4SCN or sulfo salicylic acid as indicator (see Ch-6). EDTA solution should be standardised against standard Zn-acetate solution in NH_4Cl - NH_3 buffer medium (pH = 10) using EBT indicator (see Ch-6).

Procedure :

- (i) Place 0.5 to 2.5 ml of the 0.001(M) Fe^{II} solution in a 25 ml volumetric flask and add 1 ml of 0.5% 1,10 phenanthroline solution make up the volume to 25 ml with 0.01(M) HNO_3 solution and mix uniformly. Measure the absorbance of the solution between 700-400 nm and hence find the λ_{max} (or the best filter in case of a colourimeter). Adjust the volume of the Fe^{II} solution to obtain the absorbance value of $\sim 0.5 - 0.7$ at the λ_{max} .
- (ii) Prepare a series of Fe^{II} solutions, each of total volume = 25 ml and acidity 0.01 (M) of known strength by mixing 0.5 to 2.5 ml 0.001 (M) Fe^{2+} solution with 1 ml of 0.5% 1,10 phenanthroline solution and diluting to 25 ml with 0.01(M) HNO_3 . Mix the solutions uniformly, measure their absorbance at the λ_{max} (or best filter) and plot absorbance against concentration of Fe^{II} . Draw the best straight line passing through the origin and the experimental points hence find the useful range of concentration where Beer's Law is obeyed.

Acidity = 0.01(M). Optical path length = 1 cm.

Set	Vol. of 0.001(M) Fe ^{II} (ml)	Vol. of 0.5% phen (ml)	Total Vol. (ml)	[Fe ^{II}](M) × 10 ⁵	Fe (ppm)	Abs.
1	0.50	1.0	25	2	1.12	—
2	1.00	1.0	25	4	2.24	—
3	1.50	1.0	25	6	3.36	—
4	2.00	1.0	25	8	4.48	—
5	2.50	1.0	25	10	5.60	—

- (iii) Place 0.5 to 2.5 ml of faintly acidic (pH = 2) 0.001(M) solution of Fe^{III} or (Fe^{II} + Fe^{III}) mixture, as the case may be in a 25 ml volumetric flask. Determine in another same volume of the sample the quantity of acetate buffer (pH ~ 4.5) required to bring the pH of the solution to ~ 3.5 (i.e., yellow colour of bromophenol blue). Add this quantity of acetate buffer to the experimental solution in the volumetric flask. Add 1 ml of 1% hydroquinone solution to reduce Fe^{III} to Fe^{II} and then add 1 ml of 0.5% 1,10 phenanthroline solution. Allow to stand for one hour. Make up the volume to 25 ml with 0.01(M) HNO₃ and measure the absorbance of the solution at the λ_{max} (or best filter). Find the concentration of Fe^{III} or total (Fe^{II} + Fe^{III}), as the case may be, from the calibration curve.
- (iv) Fe^{II} alone can be determined in the sample solution in the presence of Fe^{III} by omitting the hydroquinone reduction step.
- (v) Finally Fe^{III} is obtained from the difference : Fe^{III} = (Fe^{II} + Fe^{III}) – Fe^{II}.

Appendix - A

Reagents Used in Quantitative Analysis

(*Normality = % strength $\times 10 \times$ Sp. Gr./ Equivalent weight)

	Concentrated Acids & Ammonia	Specific gravity	Percent by weight	Approximate Normality*
1.	Acid Acetic (glacial)	1.05	99.5	17(N)
2.	Acid Hydrochloric (conc.)	1.19	38	12(N)
3.	Acid Nitric (conc.)	1.42	70	16(N)
4.	Acid Sulphuric (conc.)	1.84	96	36(N)
5.	Acid Sulphuric (conc.)	1.84	98	36.8(N)
6.	Acid Phosphoric (syrupy)	1.69	85	45(N)
7.	Liquor Ammonia	0.88	28	15(N)
	Dilute Acids	Approximate Normality	Preparation of the Reagents	
8.	Acid Acetic (dilute)	5(N)	Dilute ~295ml of glacial acetic acid to 1000ml of distilled water	
9.	Acid Hydrochloric (dilute)	5(N)	Dilute ~420ml concentrated HCl to 1000ml by distilled water	
10.	Acid Nitric (dilute)	5(N)	Dilute ~315 ml concentrated HNO ₃ to 1000ml by distilled water	
11.	Acid Sulphuric (dilute)	5(N)	Add~140 ml. of conc. H ₂ SO ₄ to ~500ml distilled water, then dilute to 1 litre	
	Dilute Alkalies	Approximate Normality	Preparation of the Reagents	
12.	Ammonia solution (dilute)	5(N)	Dilute 335ml liquor NH ₃ to 1000ml by distilled water	
13.	Sodium Hydroxide (dilute)	5(N)	Dissolve ~200-220 g NaOH in distilled water and dilute to 1000ml.	
14.	PotassiumHydroxide (dilute)	5(N)	Dissolve ~280-300 g KOH in distilled water and dilute to 1000ml.	
15.	Alcoholic Potassium Hydroxide	0.5(N)	Dissolve ~ 30 g. of (A.R.) KOH in 20 ml of distilled water and then make up the final volume to 1 litre using 95% ethanol.	

Some Common Reagents	Approximate Strength	Preparation of the Reagents
16. Stannous Chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$)	15%	Dissolve 30 g. of A.R crystalline $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 100 ml conc. HCl by heating and dilute to 200ml with distilled water.
17. Mercuric Chloride (HgCl_2)	5%	Dissolve 50 g of A.R. HgCl_2 in distilled water and dilute to 1000ml.
18. Mohr's Salt solution :	0.1N	Dissolve 39.2 g. of A. R. Mohr's salt in 500ml of 4 (N) H_2SO_4 and then dilute to 1 litre with distilled water and cool to room temperature.
19. Sodium thiosulfate solution,	0.1N -	Dissolve about 24.8 g. of A.R. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in 500ml boiled out cooled distilled water and dilute to 1 litre add 3 drops of CHCl_3 to improve the stability of the solution and store in amber coloured bottle.
20. Zimmermann-Reinhardt (Z-R) Reagent	-	Mix carefully 100 ml of concentrated H_2SO_4 to 300 ml distilled water, cool to room temperature. Dissolve 50 g of A.R. crystalline $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ in it, add 100ml of syrupy H_3PO_4 and mix uniformly.
21. Buffer solution of pH 10	-	Dissolve 17.5 g of A.R. NH_4Cl in 142 ml of conc. ammonia solution (Sp.gr. 0.88-0.90) and dilute to 250ml with distilled water.
22. Fehling's Solution – A	-	Dissolve 34.6g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 500ml of distilled water followed by adding a few drops of dilute H_2SO_4 .
23. Fehling's Solution – B	-	Dissolve 175 g of Rochelle salt and 70 g of NaOH in 500 ml of distilled water.
24. Silver nitrate	0.1(M)	Dissolve ~ 17 g of AgNO_3 in double distilled water, dilute to 1litre and mix uniformly. Preserve in a dark coloured bottle away from light.
25. Iodine Solution	0.1(N)	Dissolve~ 2 g. of iodate free KI in 20 ml of distilled water in a 250 ml stoppered conical flask and add 8 g. of resublimed iodine in it. Stopper the flask and shake to dissolve the iodine and finally dilute to 100 ml with distilled water.

	Some solid Reagents	Formula Weight (C ¹² =12.000)	Equivalent Weight
26.	Potassium dichromate	294.185	49.03
27.	Potassium permanganat	158.034	31.6 (In acid medium)
28.	Potassium bromate	167.001	27.8335
29.	Oxalic acid, H ₂ C ₂ O ₄ ·2H ₂ O	126.066	63.033
30.	Sodium oxalate Na ₂ C ₂ O ₄	133.978	66.989
31.	Sodium thiosulfate, Na ₂ S ₂ O ₃ ·5 H ₂ O	248.186	248.186
32.	Mohr's salt, (NH ₄) ₂ SO ₄ ·FeSO ₄ ·6H ₂ O	392.143	392.143
33.	Calcium carbonate, CaCO ₃	100.087	50.0435
34.	Magnesium carbonate, MgCO ₃	84.314	42.157
35.	Hydrogen peroxide, H ₂ O ₂	34.015	17.0075
36.	CuSO ₄ ·5H ₂ O	249.6864	249.6864
37.	Potassium biiodate, KH(IO ₃) ₂	389.912	32.4927(as oxidant) 389.912 (as acid)
38.	Na ₂ H ₂ EDTA·2H ₂ O	372.22	372.22
39.	Zn(CH ₃ COO) ₂ ·2H ₂ O	219.38	219.38
40.	MnO ₂	86.937	43.47 (in acid solution)
Gravimetric Factors of Some Precipitates			
	Precipitated as	Weighed as	Gravimetric Factor
41.	Ni(DMGH) ₂ Bis-dimethylglyoximato Ni(II)	Ni(C ₄ H ₇ O ₂ N ₂) ₂	0.2032
42.	CuSCN	CuSCN	0.5224
43.	BaSO ₄	BaSO ₄	0.58845
44.	AgCl	AgCl	0.2474

	Some Common Indicators	Approximate Strength	Preparation of the Indicator
45.	Phenolphthalein (pH range: 8.3-10)	~0.5%	Dissolve 0.5 g of the dyestuff in 100 ml 1:1 ethanol.
46.	Methyl orange (pH range: 3.1- 4.4)	~0.05%	Dissolve 0.05 g of the dyestuff (free acid) in 100 ml water and filter if necessary.
47.	Bromo-cresol green (pH range: 3.8- 5.4)	0.1%	Dissolve 0.1 g of the dyestuff in 100 ml ethanol.
48.	Methyl red (pH range: 4.2-6.3)	0.1%	Dissolve 0.1 g of the dyestuff in 60 ml ethanol and dilute with 40 ml water.
49.	Ba-/ Na- diphenylamine sulphonate	0.2%	Dissolve 0.2 g of the dyestuff in 100 ml water.
50.	Starch Solution	1%	Make a paste of 1 g of soluble starch with a little water and pour it into 100 ml boiling water with constant stirring. Then boil for 1 minute. Use 2 ml of the indicator solution per 100 ml of the titrating solution.
51.	Eriochrome Black T (or Solochrome Black)	(a) 0.4% solution (b) 1.0% solid reagent	(a) 0.4% methanolic solution, stable for about a month. (b) Grind a mixture of 0.05 g dyestuff with 5.0 g of A.R. KNO ₃ or KCl or NaCl. Use ~50 mg indicator mixture per titration.
52.	Xylenol orange	(a) 0.5% solution (b) 1.0% solid reagent	(a) 0.5% aqueous solution. The solution is stable for a long time. (b) Grind a mixture of 0.05 g dyestuff with 5.0 g of A.R. KNO ₃ or KCl or NaCl. Use ~50 mg indicator mixture per titration.
53.	Patton and Reeder's Indicator	1.0%	Grind a mixture of 0.05 g dyestuff with 5.0 g of A.R. KNO ₃ or KCl or NaCl. Use ~1.0 g indicator mixture per titration.
54.	Murexide	0.2%	Grind a mixture of 0.1 g dyestuff with 5.0 g of A.R. KNO ₃ or KCl or NaCl. Use 0.2-0.4 g indicator mixture per titration.
55.	Calcon (Solochrome Dark Blue)	0.4%	0.4% methanolic solution.
56.	PAN [1-Pyridyl-(2-azonaphthol)]	0.05%	Dissolve 0.1 g of dye staff in 50 ml of ethanol or methanol.



Appendix – B

List of U.G. Experiments on Quantitative Chemical Analyses, Organic Reactions, Chromatographic Separations and Physicochemical Experiments included in the revised Syllabus (2002) of three year B.Sc. (General & Honours) Degree Courses in Chemistry of the University of Calcutta.

B.Sc. General Course (Part – II)

Paper – IV : (B) Practical (25M) (75-90L) Unit – 1 : Quantitative Chemical Analysis :

Page

Experiment – 1

- (i) Preparation of standard (N/20) solution of oxalic acid and standardization of (a) NaOH solution, (b) KMnO_4 solution, (c) Mohr's salt solution (against KMnO_4). ... 23,47,48
... 24,26
- (ii) Preparation of standard (N/20) Na_2CO_3 solution and standardization of $\text{HCl}/\text{H}_2\text{SO}_4$ solution.

Experiment – 2

- Preparation of standard (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution and standardization of ... 73,48,75
(a) Mohr's salt solution, (b) KMnO_4 solution, (c) Sodium thiosulfate solution.

Experiment – 3

- Preparation of (M/50) zinc acetate solution and standardization of $\text{Na}_2\text{H}_2\text{EDTA}$ solution. ... 109

Experiment – 4

- (a) Acidimetric estimation of NaHCO_3 and Na_2CO_3 mixture. ... 24
(b) Determination of alkali content of antacid tablet using HCl 283
(c) Estimation of acetic acid in commercial vinegar using NaOH 286

Experiment – 5

- (a) Estimation of unknown solution containing single metal ion ($\text{Zn}^{2+}/\text{Ca}^{2+}/\text{Mg}^{2+}$) by EDTA titration. ...109,110
(b) Estimation of total hardness of water samples by EDTA titration. ... 249

Experiment – 6	Page
Estimation of (a) (NH_4^+) , (b) Aminoacid (glycine/ α -alanine) by Sorensen formol titration.	... 256,258
Experiment – 7	
Titrimetric estimation of glucose using Fehling's solution.	... 261
Experiment – 8	
Estimation of dissolved oxygen in water samples.	... 281
Experiment – 9	
Estimation of urea by hypobromite method.	... 268
Experiment – 10	
Estimation of formalin	... 278
Experiment – 11	
(i) Estimation of $\text{Fe}^{\text{II}} + \text{Fe}^{\text{III}}$ mixture using standard (N/20) solution (a) $\text{K}_2\text{Cr}_2\text{O}_7$, (b) KMnO_4 as titrants	... 81,51
(ii) Iodometric estimation of copper using thiosulfate	... 83,89
Experiment – 12	
Estimation of available oxygen in pyrolusite.	... 68
Experiment – 13	
Estimation of saponification value of ester/oil/fat.	... 252
Experiment – 14	
Estimation of available chlorine in bleaching powder.	... 254
Experiment – 15	
Estimation of Vitamin C (reduced).	... 265
Experiment – 16 : Demonstration Experiments (may be done in groups).	
(a) Crystalization of organic compounds (benzoic acid, acetanilide) from hot/boiling water.	
(b) Decolourization of coloured sugars using active charcoal and crystallization	
(c) Setting up of glass distillation apparatus using condenser and preparation of distilled water.	



B.Sc. Part – I Honours – Paper – IV : (Practical)

Unit – 1 : Physicochemical Experiments : (20 M) (75 L)

Physical Chemistry Experiment

<i>Experiment – 1 :</i>	Page
Determination of solubility of a given substance in water at different temperatures and construction of its solubility curve.	... 185
<i>Experiment – 2 :</i>	
Determination of surface tension of a given liquid/solution by drop weight method.	... 187
<i>Experiment – 3 :</i>	
Determination of viscosity coefficient of a given liquid/ solution with Ostwald's viscometer.	... 188
<i>Experiment – 4 :</i>	
Determination of distribution coefficient of an organic acid between water and an organic solvent	... 190
<i>Experiment – 5 :</i>	
To determine the pH of a given buffer solution by colour matching of indicator.	... 193
<i>Experiment – 6 :</i>	
To determine the rate constant of a first order reaction (acid hydrolysis of ester by titrimetric method)	... 196
<i>Experiment – 7 :</i>	
To determine the solubility product of a sparingly soluble salt by titrimetric method.	... 198
<i>Experiment – 8 :</i>	
To determine the partition co-efficient of iodine between water and an organic solvent.	... 200
<i>Experiment – 9 :</i>	
To determine the equilibrium constant of the reaction : $\text{KI} + \text{I}_2 \rightleftharpoons \text{KI}_3$ by partition method. (Partition co-efficient to be supplied).	... 202
<i>Experiment – 10 :</i>	
To determine the rate constant of decomposition of H_2O_2 by acidified KI solution using clock reaction.	... 205



B.Sc. Part-II Honours – Paper – VII (Practical)

Unit – 1 : Advanced Physical Chemistry Experiments : (50 M) 200 L)

<i>Experiment – 1 :</i>	Page
To determine the specific rotation of a given optically active compound and hence to determine the % composition of its aqueous solution using polarimeter.	... 208
<i>Experiment – 2 :</i>	
To study the kinetics of inversion of cane sugar using polarimeter.	... 210
<i>Experiment – 3 :</i>	
To determine the concentrations of each of HCl and CH ₃ COOH in a mixture conductometrically using standardized caustic soda solution.	... 215
<i>Experiment – 4 :</i>	
To study the kinetics of saponifications of ester by conductometric method.	... 218
<i>Experiment – 5 :</i>	
(a) To determine the ionisation constant of a weak acid by conductometric method,	... 222
(b) To determine the solubility and solubility product of a sparingly soluble electrolyte by conductometric method.	... 224
<i>Experiment – 6 :</i>	
To titrate potentiometrically the given ferrous ammonium sulphate solution using K ₂ Cr ₂ O ₇ /KMnO ₄ as standard and hence to find the redox potential of Fe ³⁺ /Fe ²⁺ system on the hydrogen scale.	... 227
<i>Experiment – 7 :</i>	
To titrate potentiometrically a standard solution of KCl against AgNO ₃ solution and hence to determine (i) the concentration of AgNO ₃ and (ii) the solubility product of AgCl.	... 230
<i>Experiment – 8 :</i>	
To test the validity of Lambert-Beer's Law for KMnO ₄ /K ₂ Cr ₂ O ₇ solution and hence to determine the concentration of the given solution of the substance.	... 233
<i>Experiment – 9 :</i>	
To determine the pK _{in} value of an acid-base indicator by colourimetric method.	... 236

	Page
Experiment – 10 :	
To study the kinetics of the reaction $I^- + S_2O_8^{2-}$ by colourimetric method.	... 238
Experiment – 11 :	
Determination of pK^H value of a weak acid by pH-metric method.	... 242
Experiment – 12 :	
To study of the phase diagram of a binary system (phenol-water) and the effect of impurities (e.g., NaCl).	... 245
Experiment – 13 :	
Writing computer PROGRAM on BASIC language and to solve the following problems using PC.	
(a) (i) Plotting Pressure Volume curve for a van der Waals gas.	
(ii) Plotting of Maxwell distribution curves for speeds of gas molecules.	
(b) (i) Calculation of molar extinction co-efficient from absorbance concentration data.	
(ii) Calculation of equilibrium constants of chemical reactions from conductometric/potentiometric/pH-metric/colourimetric data (any one).	
(iii) Calculation of rate constants of chemical reactions from concentration vs. time/conductance vs. time/absorbance vs. time data (any one).	
 Unit – 2 : Quantitative Estimation of Single Compound/Constituent/Parameter & Demonstration Experiments (25 M) (120 L)	
Experiment 1 :	
Estimation of total hardness of water sample (complexometric EDTA method)	... 249
Experiment 2 :	
Estimation of saponification value of oil/ester fat.	... 252
Experiment 3 :	
Determination of available chlorine in bleaching powder	... 254
Experiment 4 :	
Determination of available oxygen in pyrolusite.	... 68

	Page
Experiment 5 :	
Determination of the strength of H_2O_2 sample.	... 70
Experiment 6 :	
(a) Estimation of NH_4^+ /amino acid by formol titration.	256,258
(b) Determination of acetic acid in commercial vinegar using NaOH.	... 286
(c) Determination of alkali content of antacid tablet using HCl.	... 283
Experiment 7 :	
Estimation of sugar (glucose/sucrose) by titration using Fehling's solutions.	261,262
Experiment 8 :	
Estimation of Vitamin C (reduced).	... 265
Experiment 9 :	
Estimation of urea (hypobromite method).	... 268
Experiment 10 :	
Estimation of phenol, aromatic amine (bromate/bromide method).	275, 272
Experiment 11 :	
Determination of ion-exchange capacity of strongly acidic cation exchange resin (column/batch method).	... 179
Experiment 12 :	
Determination of Na^+/K^+ ion in a given solution by ion exchange method.	... 289
Experiment 13 :	
Estimation of Ca (a) in milk powder, or, (b) in chalk (EDTA method).	294, 292
Experiment 14 :	
Colourimetric estimation of Mn in a given solution sample / commercial H_3PO_4 sample.	... 298
Experiment 15 :	
Colourimetric estimation of P in a given solution sample.	... 300
Experiment 16 :	
Demonstration Experiment (may be done in groups). Setting up of glass distillation set and preparation of conductivity water (to be tested by conductance and pH measurements).	



B.Sc. Part-II Honours Paper – VIII (Practical)

Unit – 1 : Quantitative Estimation of the Constituent(s) of Mixtures/Complex Materials (Inorganic Samples) (50 M) (200 L)

Page

Experiment – 1 : Gravimetric estimation of

(a) Water of crystallisation of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ 5
(b) Chloride as AgCl 7
(c) Sulphate or Ba as BaSO_4 9, 11
(d) Phosphate or Pb as $\text{Pb}_3(\text{PO}_4)_2$ 13
(e) Cu as CuSCN 15
(f) Ni as Ni (DMGH)_2 17

Experiment No. 2 : Titrimetric Estimations Based on Acidimetry- Alkalimetry:

(a) Preparation of (N/20) oxalic acid and (N/20) Na_2CO_3 solutions and standardization of (i) NaOH , (ii) HCl and (iii) CH_3COOH using indicators.	... 23
(b) Estimation of (i) NaHCO_3 and Na_2CO_3 mixture, (ii) Na_2CO_3 and NaOH mixture.	... 24, 25

Experiment No. 3 : Redox Titrimetric Estimations Based on Permanganometry

(a) Preparation of (N/20) oxalic acid/sodium oxalic and standardization of (i) KMnO_4 solution, (ii) Mohr's salt solution.	... 47, 48
(b) Estimation of (i) Fe^{II} and Fe^{III} in mixture, (ii) CaCO_3 in dolomite, (iii) Total Mn in pyrolusite, (iv) Fe and Ca in mixture, (v) CaO and Fe_2O_3 in Portland cement, (vi) Mn in cast iron/steel, (vii) MnO in basic slag.	... 51, 52, 55, 59, 63, 62, 67, 66

Experiment No. 4 : Redox Titrimetric Estimations using standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution.

(a) Preparation of (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution and standardization of (i) Mohr's salt solution, (ii) Sodium thiosulfate solution.	... 73, 75, 77
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- (b) Estimation of (i) Fe^{II} and Fe^{III} in mixture, (ii) Cu in brass/chalcopyrites, ... 81,83,85,
 (iii) Fe and Cu in mixture, (iv) Fe and Cr in mixture, (v) $\text{Fe(III)} - \text{Cr}_2\text{O}_7^{2-}$ 87,89,92,
 in mixture, (vi) Fe and Mn in mixture, (vii) Fe_2O_3 in Portland cement/ 95, 100,
 basic slag.

Experiment No. 5 : Titrimetric Estimations Based on Complexometric EDTA Titration.

- (a) Preparation of (M/50) zinc acetate solution and standardization of ... 109
 $\text{Na}_2\text{H}_2\text{EDTA}$ solution.
 (b) Complexometric estimation of (i) Ca and Mg in mixture, (ii) Fe ... 110,
 and Al in mixture, (iii) Total ($\text{CaCO}_3 + \text{MgCO}_3$) in dolomite, 114,115,117,
 (iv) Fe and Ca in mixture. 119,121,124

Unit – 2 : Typical Organic Reactions/Chromatographic Separations & Demonstration Experiments (25 M) (120 L)

Experiment No. 1 : Typical Organic Reactions

Isolation, purification and m.p./b.p. (as the case may be) determination of the product (solid/liquid).

- (i) Nitration of aromatic compounds. ... 132
 (ii) Condensation involving elimination of $\text{H}_2\text{O}/\text{NH}_3$ 136
 (iii) Hydrolysis of amide/imide/ester. ... 138
 (iv) Reduction of (a) aromatic nitro compounds. (b) Carbonyl/Compounds ... 142,144
 (v) Side chain oxidation of aromatic compounds ... 145
 (vi) Diazotisation and coupling reactions. ... 147
 (vii) Esterification. ... 151
 (viii) Halogenation of aromatic compounds. ... 157
 (ix) Acetylation. ... 153
 (x) Benzoylation of phenols and aromatic amines. ... 155

Experiment No. 2 : Chromatographic Separations, Determination of R_f Values and Identification of Organic Compounds.

(a) <i>TLC separation</i> :	(i) Amino acids : mixtures of 2/3 amino acids	... 168
	(ii) Mixture of dyes	... 170
	(iii) Leaf pigments from spinach leaves	... 171
(b) <i>Column chromatographic separation</i> :		
	(i) Leaf pigments from spinach leaves	... 173
	(ii) Mixtures of dyes (fluorescein and methylene blue)	... 174
	(iii) Resolution of racemic mixture of (-*) mandelic acid	... 175
(c) <i>Paper chromatographic separation</i> :		
	(i) Sugars (mixtures of 2/3 sugars)	... 167
	(ii) Mixture of 2/3 amino acids	... 163
	(iii) Leaf pigments from spinach leaves.	... 165

Experiment No. 3 : Demonstration Experiments (may be carried out in groups)

- (i) Determination of boiling point of organic liquid (ethanol/cyclohexane/benzene/toluene).
- (ii) Collection of ethanol by distillation of ethanol-water mixture using water condenser. Distillation and collection of nitrobenzene/aniline using air condenser.
- (iii) Steam distillation (naphthalene from its suspension in water/clove oil from cloves/*o*- and *p*-nitrophenols).